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The Activity and Other Thermodynamic Properties of Hydrochloric Acid in Tetrahydrofuran - Water Mixtures.

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THE ACTIVITY AND OTHER THERMODYNAMIC PROPERTIES OF HYDROCHLORIC ACID IN TETRAHYDROFURAN-WATER MIXTURES

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ABSTRACT

Much interest in the study of the thermodynamic properties of mixed-aqueous organic solvent has developed recently due to its tremendous importance and its application to Physical as well as Analytical Chemistry. A systematic study of different mixed-solvent systems seems appropriate for the classification of solvents according to their dielectric properties, miscibility with water, primary and secondary medium effects, and other thermodynamic properties.

Activity and other thermodynamic properties of hydrochloric acid were determined from the electromotive force measurements of the cell Pt, H_2 (1 atm.)| HCl (m), Tetrahydrofuran, Water| AgCl, Ag over a wide range of solvent compositions and hydrochloric acid molalities at 0°, 15°, 25° and 35°C. The standard electrode potentials, E° values were evaluated for each system by extrapolation of the curve formed by plotting the quantity E', which corresponds to $E_{obs} + \frac{2RT}{F} \ln m$, as ordinate and $m^{\frac{1}{2}}$ as abscissa. The extrapolations were carried out by using the standard form of the polynomial curve fitting program. It was shown that these data were represented by straight lines at the lower concentrations, and that the extrapolation could be made with high precision. An equation very similar to that used in the polynomial curve fitting program was derived by the application of LaMer, Gronwall extension of the Debye and Hückel theory.

A comprehensive study of the mean activity coefficients of hydrochloric acid and other thermodynamic properties such as primary and secondary medium effects, the relative partial molal heat content

and heat capacity, etc. was made from electromotive force measurements. These thermodynamic properties followed the general trends as seen in other mixed solvent systems. There is evidence of ionic association at higher concentrations of tetrahydrofuran.

The accuracy of e.m.f. measurement is of the order of ± 0.05 millivolt for 8.98 and 18.21 percent tetrahydrofuran and ± 0.5 millivolt for higher concentrations of tetrahydrofuran.

CHAPTER I

INTRODUCTION

Much progress has been made in regard to the thermodynamic properties of the mixed-solvents after the advent of Debye-Hückel theory (31) which leads to exact relations from which the behaviors of dilute solutions of electrolytes may be quantitatively predicted.

The thermodynamic properties of electrolytes can be divided mainly into two groups:

(a) those determined by measurements of systems which are in equilibrium, and

(b) those determined by measurements of systems in the disturbed states.

Reversible thermodynamics provides the method for treating the systems in equilibrium. In our research program, we have derived the thermodynamic properties from measurements of electrode potentials of the galvanic cells.

The properties of hydrochloric acid in aqueous, non-aqueous and also in mixed solvent systems have been studied in considerable detail and these may be used to illustrate the chief characteristics of ionic solutions.

In studying chemical equilibria, precipitation reaction, chelate compound formation, organic preparations, solubility, chemical kinetics, quantitative analysis, etc., it is sometimes found necessary to use mixed solvents mainly to avoid hydrolysis, insolubility, and other complicating features. An interesting application of the use of mixed

solvent is reported by Shuman and Sen (43) in their studies of the complex formation thermodynamics of some metal (II) phenyl-2-pyridylketoximates. A second example is the study of conductance in dioxane-water mixtures by Owen and Waters (40). Another classic example of the use of mixed solvent is due to Kraus and Fuoss (33) in their conductance studies with subsequent interpretation of the results in terms of ionic association. However, the use of mixed solvents creates the very fundamental problem of determining the proper reference state. Usually, the thermodynamic properties of solutes measured in a given mixed solvent have the reference state defined by infinite dilution in the mixed solvents. The relative thermodynamic properties in a given mixed solvent system referred to the mixed solvent are important. However, it would be of considerable importance if the values of these properties were known relative to the standard reference aqueous state.

One of the purposes of this research program is to find out the means of converting the values obtained from the mixed solvent systems to those of the standard reference aqueous state, i.e., to find out a proper correction factor which corresponds to the free energy change involved in transferring the reacting solutes from aqueous solution to the mixed solvent. This has been termed by Owen (3, 39) as the primary medium effect. In order to apply these corrections, the primary and secondary medium effects (39) must be known. If we study the formation of a complex in a mixed solvent, we must know the complex formation thermodynamics (32) in infinitely dilute mixed solvent system for the application of the above correction.

For a number of reasons, tetrahydrofuran was selected as the

organic component of the mixed solvent system. There has been a considerable interest shown in the use of tetrahydrofuran after it was recommended by DuPont (13) as an excellent organic solvent for the common usage. Since tetrahydrofuran is completely miscible with water, it not only serves as a solvent for investigating the properties of the various solutes in it, but as well can be utilized to know the properties of the solutes in mixed solvents. Hence, in view of the importance of tetrahydrofuran in its application in various fields it was desired to measure and calculate different thermodynamic properties, not only in pure state, but also in its various mixtures with water having different composition in presence of hydrochloric acid as an electrolyte over some temperature ranges. If the thermodynamic properties of hydrochloric acid in this mixed solvent system are known, then these might be of fundamental importance in determining the appropriate correction factor to be used for treating the mixed solvent data. Comparison of the results obtained from electromotive force measurement can be made with the results obtained from calorimetric measurement. In this manner, a comprehensive view of the properties of a single electrolyte as a function of the temperature, concentration, activity coefficients, etc. is obtained. All these results will be discussed in detail in relation to the predictions of the interionic attraction theory as well as by the extended terms of the Debye and Hückel theory according to Gronwall, LaMer and Sandved (16) and also LaMer, Gronwall and Grieff (36).

The following galvanic cell has been used in the study of the mixed solvents.

Pt, H_2 (1 atm.)| HCl(m), THF (X), Water (Y)| AgCl-Ag 1

in which m represents the molality of the hydrochloric acid, THF stands for tetrahydrofuran, X and Y are the weight percent of tetrahydrofuran and water, respectively.

Harned and his coworkers (17-29) made a comprehensive study in the measurement of electromotive forces of such cells using different mixed solvent, of which dioxane-water mixture is the interesting one. These include accurate measurements of the cells at 5° intervals over a wide range of temperature, from $0^{\circ}C$ to $50^{\circ}C.$, at the concentrations of hydrochloric acid ranging from 0.001 molal to the highest practical concentrations in 20, 45, 70 and 82 percent dioxane-water mixtures, which correspond to the values of the solvent dielectric constant of about 60, 40, 20 and 10. These values of the dielectric constants in the mixed solvent have been determined by Akerlöf and Short (11). The electromotive force data can be reproduced to within ±0.01 millivolt except when the dielectric constant of the mixed solvent decreases; or in other words, when the solutions of the mixed solvent are more concentrated in dioxane. The experimental results for solutions of low percentage of dioxane were within the limit of ±0.02 millivolt. There are several methods for the determination of the standard electrode potentials by extrapolations. For the evaluation of the standard electrode potentials in the lower concentrations of dioxane, i.e., 20 and 45 percent of dioxane in the mixture, Debye and Hückel limiting equation without using the term for the mean distance of closest approach (3) was adopted. The second extrapolation method

was the Gronwall-LaMer extension of the Debye and Hückel theory (16). In the lower concentration of dioxane (20 percent), both of these methods gave almost the same results for the standard potentials, since the contribution of the extended terms in the case of the 20 percent solution is very small. All extrapolations were made graphically. As the dielectric constant of the solvent decreases, the effect of the higher order terms of the interionic attraction theory (3), must be given priority in the extrapolations, since the difference between the results of the two extrapolation methods become greater (0.7 millivolt) for 45 percent dioxane and approximately 2 mv for 70 percent dioxane (18). The evaluation of the standard potential in solutions of dielectric constant as low as those containing 82 percent dioxane cannot be carried out with accuracy. The important reason is that the Gronwall, LaMer and Sandved extension of the Debye and Hückel theory (17, 22) is not very satisfactory in a media having dielectric constant of the magnitude 10 or less, since the second term of the extended theory is large. Hence, in view of the above difficulties, a new method which involved the law of mass action and ionization data derived from conductance measurements, was utilized at a low acid concentrations (29). This procedure is not very satisfactory but better than other methods. Hydrochloric acid, a strong electrolyte, behaves as a weak electrolyte in a low dielectric constant of the solvent.

The results of the electromotive force data were expressed by the equation over a wide range of temperature

$$E = E_{25} + a\,(t-25) + b\,(t-25)^2 + \ldots \qquad \ldots.2$$

in which E represents the electromotive force of the cell at temperature t in degree centigrade, E_{25} is the electromotive force of the cell at 25°C.; the values of the constants a and b have been determined by the method of least squares. The values of the mean activity coefficients at each rounded concentrations of hydrochloric acid in different compositions of the mixed solvent were computed at different temperatures. A plot of the logarithm of the mean activity coefficient versus square root of the molality gives sufficient information in regard to ionic association in the various composition of the solvents, i.e., for 0, 20, 45, 70 and 82 percent dioxane. An elaborate discussion has been furnished by reference (3). The most important feature of the results is that these values are in good agreement with those predicted by the Debye and Hückel theory in dilute solutions. The observed plot lies above the limiting slope of the Debye and Hückel theory provided that there is no ionic association. This is due to the fact that the theory includes the mean distance of approach of the ions. In media containing 0, 20, and 45 percent dioxane, the results confirm with this prediction, and at all concentrations lie above the limiting slope. The observed plot superimposed with the limiting slope for 70 percent dioxane mixture. In the 82 percent dioxane mixtures, the observed plot lies below the limiting slope indicating thereby that ionic association occurs. The mean activity coefficients at all concentrations and temperatures decrease with increasing temperature, hence, the relative partial molal heat content, $\bar{L}_2$, has positive values in each case. The following procedures were adopted for these calculations. The electromotive force data, E', which is equal to

$E_{obs} + \frac{2RT}{F} \ln m$, were first plotted against the square root of the molality, and then the smoothed values for E_{obs} were taken from the graph at rounded concentrations. The coefficients of equation (3) were determined by using the method of least squares at rounded concentration of hydrochloric acid;

$$E_{obs} = a + bT + cT^2 \qquad \ldots.3$$

The standard electrode potential, E^o, was determined by extrapolation from the plot of E' versus $m^{\frac{1}{2}}$. The values of the constants, a_o, b_o, c_o, were also determined from the following equation by the method of least squares.

$$E_o = a_o + b_oT + c_oT^2 \qquad \ldots.4$$

The characteristic behavior of the relative partial molal heat content as a function of the dielectric constant is understood when we plot experimental values, $\bar{L}_2$, against root molality. As the dioxane content of the mixture increases, there is an increasing tendency for the experimental curves to be higher than the limiting values in the dilute solution. All the curves have similar characteristics, first rapid rise in dilute solutions, then the decrease in slopes and finally, they rise again as the solutions are getting concentrated.

The calculations of the relative partial molal heat content, $\bar{L}_2$, and relative partial molal heat capacity, $\bar{J}_2$, from electromotive force measurements are very sensitive to experimental errors. An error of about ± 7 cal. for $\bar{L}_2$ is obtained if the temperature coefficient of electromotive force is determined within ± 0.001 mv/deg. Calorimetric values are better than those of electromotive force where an accuracy

of ±30 cal. is considered to be satisfactory.

The relative partial molal heat capacity, $\bar{J}_2$, can be determined for hydrochloric acid but not with sufficient accuracy since the determination of $\bar{J}_2$ involved the second differential coefficient of the original electromotive force data. The error is of the order of about ±10 cal. for highest concentration (82 percent) of dioxane.

The electromotive force of the cells in various mixed aqueous organic solvent such as methanol-water (27), ethanol-water (19-20), 2-propanol-water (19, 20, 38), glycerol-water (37), ethylene-glycol-water (12, 34), sucrose-water (42) and d-glucose-water (44) have been determined with sufficient accuracy in dilute solutions for a precise determination of the standard potentials. The mean activity coefficients were evaluated in each case and relative partial molal quantities were also calculated in some cases.

CHAPTER II

THEORY

The Nernst Equation:

To give a thermodynamic description of a system in which a chemical reaction is taking place, a general chemical reaction in the galvanic cell at constant temperature and pressure may be written in the form

$$n_a A + n_b B = n_c C + n_d D \qquad \ldots.5$$

in which n_a, n_b, n_c and n_d are the number of moles of A, B, C and D, respectively.

The total free energy change in terms of the activities of the reactants and products is given by equation (6).

$$\Delta F = \Delta F^{O} + RT \ln \frac{(a_C)^{n_c} \; (a_D)^{n_d}}{(a_A)^{n_a} \; (a_B)^{n_b}} \qquad \ldots.6$$

in which ΔF is the total free energy change, and ΔF^{O} is the standard state free energy change, i.e., when the activities of all reacting and resulting species are unity.

The equation (6) can be written as

$$\Delta F = \Delta F^{O} + RT \ln \frac{\pi' a}{\pi a} \qquad \ldots.7$$

in which $\pi' a$ and πa are equal to the activity products of the resultants and reactants, respectively.

In dealing with electrolytic solutions it will be more convenient to use the activities of the different ionic species into which the electrolyte dissociates. There is a serious difficulty in using such

a procedure. There is no way of measuring the individual ion activities.

Let us consider an electrolyte that dissociates as

$$C_{\nu^+} A_{\nu^-} \rightarrow \nu_+ C^+ + \nu_- A^- \qquad \ldots.8$$

in which $C_{\nu^+} A_{\nu^-}$ is the electrolyte, ν^+ and ν^- are the number of cations and anions, respectively, and $\nu = \nu_+ + \nu_-$. We then write the activity of the electrolyte as

$$a = a_+^{\nu_+} \; a_-^{\nu_-} = a_\pm^{\nu} \qquad \ldots.9$$

in which a is the activity of the electrolyte, a_+ = ionic activity of the cation, a_- = ionic activity of the anion and $a_\pm$ is called the mean activity of the ions.

The Activity Coefficient:

Deviations from the ideal state are expressed in terms of the activity coefficient. This is defined as

$$\gamma_\pm = \frac{a_\pm}{m_\pm} \qquad \ldots.10$$

in which $\gamma_\pm$ is the mean activity coefficient, $m_\pm$ is the mean molality of the solute. Now, according to our chosen standard state, as $m_\pm \rightarrow 0$, $a_\pm \rightarrow m_\pm$ and $\gamma_\pm \rightarrow 1$. Hence, we can say that in the case of electrolytes, the activity coefficient will be a measure of the non-ideality of the system due primarily to ion-ion interactions.

Equation (7) can be written as

$$\Delta F = \Delta F^o + RT \ln \frac{\pi' \gamma_\pm \pi' m_\pm}{\pi \gamma_\pm \; \pi m_\pm} \qquad \ldots.11$$

The Thermodynamics of Galvanic Cells:

It has been shown, that at constant temperature, pressure and composition, the free energy change is related to the reversible electrical work according to the following equation;

$$(dF)_{P,T,n} = (\psi' - \psi'')\, de \qquad \ldots.12$$

The difference $(\psi' - \psi'')$ is the electrical potential between two pieces of identical metal connected to the two reversible electrodes which are also connected by a solution of appropriate electrolytes; de is the charge transferred, and dF is the change in free energy of the reaction in a galvanic cell. Equation (12) is valid for reversible changes only and the criteria for reversibility are:

(i) No changes take place within the cell without the passage of the current.

(ii) Every change occurring during the passage of the current may be reversed by reversing the direction of the current.

Furthermore, a cell is valuable for thermodynamic investigations only when the net result of all the chemical changes which take place is known.

When all these conditions are fulfilled, then we can measure the reversible electrical work, $(\psi' - \psi'')de$, and, hence, the free energy change, dF, of a known reaction. If a cell with an electromotive force, $\pm E$, is exactly balanced against an external electromotive force, so that no charging or discharging of the cell is taking place, then $\pm E$ is the electromotive force of the cell when the entire system is in equilibrium. If the cell is imagined to

discharge against this electromotive force until a quantity of electricity, de, has passed through, the cell process will have taken place reversibly, performing the reversible electrical work, ±E de. The difference in potential, $(\psi' - \psi'')$, is equal to ±E depending on the convention adopted concerning the sign of the electromotive force. Equation (12) can now be written as

$$(dF)_{P,T,n} = \pm E\, de \qquad \ldots.13$$

In dealing with chemical reactions, the changes involved are usually expressed on a molar scale. Hence, for the passage of a Faraday, F, of electricity, or a simple multiple of a Faraday, NF is substituted for de and the following equation is obtained.

$$(\Delta F)_{P,T,n} = -NFE \qquad \ldots.14$$

In writing the equation (14), the convention of Lewis and Randall (12) is adopted; a positive E corresponds to a decrease in free energy. Substituting equation (14) into equation (11), we obtain the Nernst equation

$$E = E^{O} - \frac{RT}{NF} \ln \frac{\pi' \gamma_{\pm} \pi' m_{\pm}}{\pi \gamma_{\pm} \pi m_{\pm}} \qquad \ldots.15$$

in which $E^{O} = -\Delta F^{O}/NF$; $E = -\Delta F/NF$, and E^{O} is termed the standard electromotive force of the cell. Obviously, E equals E^{O} when the activities of all constituents are equal to unity. The composition of the solid component of the cell is ordinarily independent of the concentration of the electrolyte solution. Therefore, it is the convention to assign the value unity to the activities of such

components, and to consider them in their standard states at all temperatures under a pressure of one atmosphere. Because of the small molal volumes of solids and liquids, they may be considered to have unity activity at any pressure of the order of one atmosphere. Since the partial pressure of a gas in a gaseous mixture is proportional to the concentration, and, furthermore, the perfect gas law may be applied for practical purposes over small pressure changes in the neighborhood of one atmosphere, the activity of a gaseous component is written equal to its partial pressure.

Determination of the Standard Electrode Potential:

The standard state for the components of a solution is normally selected in such a way so that the molality is equal to activity or in other words, the activity coefficient approaches unity for each solute at infinite dilution.

In studying the thermodynamic properties of electrolyte solutions, the standard state potential as well as the activity coefficients of the solute are of fundamental importance. It is possible to determine the activities and the activity coefficients of the electrolyte used in the cell, if the value of the standard electrode potential is known. In order to study the thermodynamic properties of a strong electrolyte such as hydrochloric acid, the following galvanic cell is used.

$$Pt, H_2 (p \text{ atm.}) \mid HCl(m) \mid AgCl\text{-}Ag \qquad \ldots.16$$

This means that the hydrogen electrode and a silver-silver chloride electrode are immersed in a solution of hydrochloric acid where m represents the molality of HCl, i.e., moles of acid per 1000 gms. of

water; and p represents the partial pressure of hydrogen gas. The half-cell reactions can be written as

$$\tfrac{1}{2}\, H_2(g) - e = H^+ \qquad \ldots.17$$

and

$$AgCl(s) + e = Ag(s) + Cl^- \qquad \ldots.18$$

This gives the over-all reaction

$$AgCl + \tfrac{1}{2}\, H_2(g) = Ag(s) + Cl^- + H^+ \qquad \ldots.19$$

The electromotive force of the cell is written as, since N = 1 (one electron),

$$E = E^o - \frac{RT}{F} \ln \frac{(a_{Ag})\ (a_{H^+})\ (a_{Cl^-})}{(a_{AgCl})\ (a_{H_2})^{\frac{1}{2}}} \qquad \ldots.20$$

Making use of the conventions regarding standard states, the activities of the silver (solid), and silver chloride (solid) can be written equal to unity, and equation (20) becomes

$$E = E^o - \frac{RT}{F} \ln \frac{a_{H^+}\ a_{Cl^-}}{(pH_2)^{\frac{1}{2}}} \qquad \ldots.21$$

E (p), the electromotive force of the cell measured at a partial pressure p of hydrogen gas, is given by equation (22).

$$E\ (p) = E^o - \frac{RT}{F} \ln a_{H^+}\ a_{Cl^-} + \frac{RT}{2F} \ln pH_2 \qquad \ldots.22$$

The electromotive force of the same cell measured at a partial pressure of hydrogen of exactly 1 atmosphere, designated as the "observed" electromotive force, is given by equation (23),

$$E\ (1) = E^o - \frac{RT}{F} \ln a_{H^+}\ a_{Cl^-} + \frac{RT}{2F} \ln 1atm. \qquad \ldots.23$$

To avoid the necessity of recording the partial pressure of hydrogen gas involved in the cell reaction, it is customary to convert E (p) to E (1). The difference between E (1) and E(p) is due to the difference in partial pressure of hydrogen and is given by the following equation.

$$E\ (1) - E\ (p) = \frac{RT}{2F} \ln \frac{760}{pH_2} \qquad \ldots.24$$

or

$$\Delta E = \frac{RT}{2F} \ln \frac{760}{P-p_s} \qquad \ldots.25$$

In equation (24), ΔE represents the quantity which must be added to E (p) to get E (1); P represents the barometric pressure and p_s is the partial pressure of the solvent. E (1) is abbreviated as E_{obs}, the observed electromotive force.

Experimentally, it is possible only to measure mean ionic activity and for a uni-univalent electrolyte such as hydrochloric acid, the following equation is obtained.

$$E_{obs} = E^o - \frac{2RT}{F} \ln a_{\pm} \qquad \ldots.26$$

or

$$E_{obs} = E^o - \frac{2RT}{F} \ln \gamma_{\pm}\, m \qquad \ldots.27$$

After rearrangement, the above equation leads to

$$E_{obs} + \frac{2RT}{F} \ln m = E^o - \frac{2RT}{F} \ln \gamma_{\pm} \qquad \ldots.28$$

At this point, several different approaches can be made to determine the E^o values. An experimental method for the determination

of E^o was developed by Lewis and Randall (4) before the advent of the Debye-Hückel theory. Since the standard state has been defined as $\gamma_{\pm} \rightarrow 1$ as $m \rightarrow 0$, it is seen that the term containing the activity coefficient disappears in equation (28). Thus, if we plot the left side of the equation (28) against some function of molality, the extrapolation is not very satisfactory since it shows a curvature at the lowest concentrations, although Lewis and Randall assumed the linearity of the left side of the equation (28) against m at infinite dilution. The most common method of extrapolation is the utilization of some form of the Debye-Hückel theory which makes it possible to supplement our experimental data with the theoretical treatment in regions of high dilution. The following equation, derived by Debye and Hückel (3) for the logarithm of the mean activity coefficient of an electrolyte can be used:

$$\ln \gamma_{\pm} = - S(f)\, \Gamma^{\frac{1}{2}} + B'm \qquad \ldots.29$$

in which $S(f)$ is a constant which represents the limiting slope of the theoretical equation and contains several factors such as the dielectric constant, temperature, etc.; B' is a constant, Γ represents the "ional" concentration and is given by the following equation

$$\Gamma \equiv \sum_{1}^{s} C_i Z_i^2 \qquad \ldots.30$$

in which C_i = concentration of the ith species; Z_i = valence of the ith ion; and i = 1, 2, ... s. If the equation (29) is combined with that of (28), and after proper rearrangement, one obtains,

$$E_{obs} + \frac{2RT}{F} \ln m - \frac{2RT}{F} S(f) \Gamma^{\frac{1}{2}} = E^{o} - \frac{2RT}{F} B'm \quad \ldots.31$$

According to this equation, a plot of the left side against m will be more nearly linear even at lower concentrations and the extrapolation to E^{o} at m = 0 can be made with high precision. However, the evaluation of the standard potential in solutions of lower dielectric constant cannot be carried out with certainty by means of equation (31). Use of an improved equation derived by Gronwall, LaMer and Sandved (16,36) also does not yield satisfactory results. Hence, a method, which involves the law of mass action and use of the dissociation constants from conductance measurements is usually employed for the determination of E^{o} in a solvent of low dielectric constants.

The most serious drawback in applying equation (31) or other expressions of similar type is the essential requirements of knowing the correct values of the dielectric constants of the solvent-mixtures.

Primary and Secondary Medium Effects:

There are two types of interactions in a solution containing electrolytes. (i) ion-solvent and (ii) ion-ion. The interaction between a given ion and a particular solvent will be different from that of the same ion and a different solvent.

We can consider the primary medium effect to be due to the difference in the solvation energies in two different solvents and is a measure of the energy involved in the transfer of an ion at an infinite dilution in one solvent to an infinite dilution of another solvent. The primary medium effect is also due to the difference in ion-solvent interactions and is independent of the solute concentration.

Secondary medium effect is defined as due to the difference in ion-ion interactions in two different solvents. This effect will, of course, be concentration dependent and can be attributed primarily to a difference in solvent dielectric constant. The total medium effect is the summation of the primary and secondary medium effects. The transfer of a solute from a finite concentration in one solvent to a finite concentration in another solvent may involve three steps:

(i) The transfer of the solute from a finite concentration in one solvent at its infinite dilution;

(ii) The transfer of the solute from one solvent at its infinite dilution to an infinitely dilute solution of the second solvent;

(iii) The transfer of the solute from an infinitely dilute solution of the second solvent to its finite concentration.

Thermodynamic Representation of the Primary Medium Effect:

To obtain the thermodynamic treatment of medium effects, let us consider a galvanic cell without liquid junction of the type already represented by equation (1).

$$Pt, H_2\ (1\ atm.)\,|\ HCl\ (m)\ THF\ (X), Water\ (Y)\,|\ AgCl, Ag \quad ....1$$

in which the mole fraction of THF (tetrahydrofuran) may vary from 0 to 1.0. If we first consider the case where mole fraction of tetrahydrofuran, i.e., X = 0; we will have the common aqueous cell represented by equation (16).

$$Pt, H_2\ (1\ atm.)\,|\ HCl\ (m)\,|\ AgCl, Ag \quad ....16$$

and its potential can be expressed by equation (27), in which E

corresponds to E_{obs}.

$$E = E^{o}_{m} - \frac{2RT}{F} \ln \gamma_{\pm} m \qquad \ldots.27$$

in which all terms have their usual physical significance.

E^{o}_{m} = Standard potential of the cell based on the molal scale.

Symbolically, the potential given in equation (27) can be represented as

$$^{w}E = {}^{w}E^{\ominus}_{m} - \frac{2RT}{F} \ln {}^{w}_{w}\gamma_{\pm} m \qquad \ldots.32$$

The superscript w denotes that the measurements are being made with water as a solvent, and the subscript w on the mean activity coefficient ($\gamma_{\pm}$) indicates that $\gamma_{\pm}$ is measured relative to unit value at infinite dilution in water.

Consider a mixed solvent, i.e., tetrahydrofuran-water mixture, there exists a choice in defining the standard state.

(i) First we consider the mixed solvent in the same way as it was done for the pure solvent, then the cell potential can be expressed as

$$^{s}E = {}^{s}E^{o}_{m} - \frac{2RT}{F} \ln {}^{s}_{s}\gamma_{\pm} m \qquad \ldots.33$$

The symbol, s, indicates that the measurements are made in solvent s, and the activity coefficients are measured relative to unit value at infinite dilution in this particular solvent. Thus, the solvent is being treated as if it were a pure solvent rather than a mixed solvent. The standard state potential will be of the same form as that of water and can be written from equation (33) as

$$^{s}E = {}^{s}E^{o}_{m} - \frac{2RT}{F} \ln {}^{s}_{s}\gamma_{\pm} - \frac{2RT}{F} \ln m$$

The $\ln {}^{s}_{s}\gamma_{\pm}$ term drops out since ${}^{s}_{s}\gamma_{\pm} \rightarrow 1$ as $m \rightarrow 0$. Hence, we obtain

$$ {}^{s}E^{o}_{m} = \underset{m\rightarrow 0}{Lt} \left[{}^{s}E + \frac{2RT}{F} \ln m \right] \qquad \ldots.34 $$

(ii) Alternatively, we might prefer to consider the mixed solvent still to be an aqueous solvent to which a portion of the organic solvent (tetrahydrofuran) has been added. Hence, we can retain the same standard state for pure water and the potential is represented as

$$ {}^{s}E = {}^{w}E^{o}_{m} - \frac{2RT}{F} \ln {}^{s}_{w}\gamma_{\pm}\, m \qquad \ldots.35 $$

Since the activity coefficient is measured relative to unit value at infinite dilution in a pure aqueous medium and not in infinite dilution of mixed solvent, ${}^{s}_{w}\gamma_{\pm}$ does not approach unity as m tends to zero in the mixed solvent. Hence, expression for the standard potential can be written from equation (35) as:

$$ {}^{w}E^{o}_{m} = \underset{m\rightarrow 0}{Lt} \left({}^{s}E + \frac{2RT}{F} \ln m + \frac{2RT}{F} \ln {}^{s}_{w}\gamma_{\pm} \right) \qquad \ldots.36 $$

Now, if we take the difference in the standard state potentials in water and the mixed solvent, i.e., subtracting equation (34) from equation (36), we obtain,

$$ \left({}^{w}E^{o}_{m} - {}^{s}E^{o}_{m} \right) = \underset{m\rightarrow 0}{Lt} \left[\frac{2RT}{F} \ln {}^{s}_{w}\gamma_{\pm} \right] \qquad \ldots.37 $$

or

$$ \left({}^{w}E^{o}_{m} - {}^{s}E^{o}_{m} \right) = \underset{m\rightarrow 0}{Lt} \left[\frac{4.606RT}{F} \log {}^{s}_{w}\gamma_{\pm} \right] \qquad \ldots.37A $$

The quantity in the right hand side of the equation (37A) represents the activity coefficient of HCl acid at infinite dilution in mixed solvent relative to unit value at infinite dilution in pure water.

At infinite dilution in both media interionic effects are absent, thus we are measuring the effect of tranferring a pair of ions from one solvent to another under conditions when there are only solvent ion interaction involved. According to Harned and Owen (2, 3, 7, 39), this is the thermodynamic representation of the primary medium effect.

The Secondary Medium Effect:

The secondary medium effect can be determined by calculating a total medium effect and then subtracting the primary medium effect. The thermodynamic expression for the total medium effect can be obtained by coupling together the aqueous and the mixed solvent cells as

$$Ag,AgCl|HCl(m),\ Water|Pt,\ H_2(1\ atm.)|HCl(m),\ THF(X),\ Water\ (Y)|AgCl,Ag \qquad ....38$$

The cell reaction will involve the transfer of the HCl from the aqueous system to the mixed solvent, but if the molality (m) of HCl is the same in both solvents, then the potential of this cell is given by

$$E_{cell} = {}^{s}E - {}^{w}E = {}^{s}E^{o}_{m} - \frac{2RT}{F} \ln {}^{s}\gamma_{\pm} - {}^{w}E^{o}_{m} + \frac{2RT}{F} \ln {}^{w}\gamma_{\pm} \qquad ....39$$

Since there are no concentration changes, i.e., ln m = ln m; the energies involved are those resulting from different degrees of

non-ideality in the two systems along with differences in ion-solvent interactions. Now equation (39) becomes,

$$E_{cell} = {}^{s}E - {}^{w}E = {}^{s}E^{o}_{m} - {}^{w}E^{o}_{m} - \frac{2RT}{F}\left[\ln {}^{s}_{s}\gamma_{\pm} - \ln {}^{w}_{w}\gamma_{\pm}\right] \quad \ldots.40$$

It is possible to put equation (40) in a better form by considering a different standard state. Subtracting equation (32) from equation (35), one obtains;

$$\begin{aligned} {}^{s}E - {}^{w}E &= {}^{w}E^{o}_{m} - \frac{2RT}{F} \ln {}^{s}_{w}\gamma_{\pm}\, m - {}^{w}E^{o}_{m} + \frac{2RT}{F} \ln {}^{w}_{w}\gamma_{\pm}\, m \\ &= -\frac{2RT}{F}\left[\ln {}^{s}_{w}\gamma_{\pm} - \ln {}^{w}_{w}\gamma_{\pm}\right] \end{aligned} \quad \ldots.41$$

Combination of the equations (37), (40), (41) and proper simplification yields;

$$\ln \frac{{}^{s}_{w}\gamma_{\pm}}{{}^{w}_{w}\gamma_{\pm}} = \operatorname*{Lt}_{m \to 0}\left[\ln {}^{s}_{w}\gamma_{\pm} + \ln \frac{{}^{s}_{s}\gamma_{\pm}}{{}^{w}_{w}\gamma_{\pm}}\right] \quad \ldots.42$$

The left hand term of the above equation represents the total medium effect according to Owen (2, 3, 39). It is total in the sense that it measures the total change in chemical potential or the energy involved in the transfer of the HCl acid from a finite concentration in one solvent to the same concentration of another solvent. The first-term on the right hand side of the equation (42) represents the primary medium effect and the last term represents secondary medium effect.

The Significance of the Secondary Medium Effect:

The term ${}^{s}_{s}\gamma_{\pm}$ in equation (42) is the activity coefficient of the

HCl acid measured at some finite concentration in the solvent s, as compared to unity at infinite dilution in that solvent. The secondary medium effect is a measure of the difference in ion-ion interactions in the two different solvents, in other words, it is a measure of the relative non-ideality of the HCl acid in the different solvents (water and mixed solvent). Hence, ${}^{s}_{s}\gamma_{\pm}$ measures the difference in the 'non-ideal' part of the chemical potential of the HCl acid at a finite concentration and at infinite dilution of the mixed solvent.

The Effect of Organic Solvent on the Ionization Constant of Weak Acid:

The addition of another liquid (non-aqueous) to water usually reduces the value of the dielectric constant. If the mixed solvent is used instead of pure water as a solvent for weak acid, the electrostatic forces between the cations and anions are increased and more opportunities are provided for the formation of covalent bonds. A decrease in the dielectric constant of the solvent should, therefore, be accompanied by a decrease in the ionization constant of a weak acid dissolved in it. It is natural, therefore, to seek some relation between the dielectric constant and the ionization constant, but before considering this, it would be well to study the free energy changes.

The free energy change on the dissociation of a weak acid is given by $\Delta\overset{o}{F} = - RT \ln K$, where K is the dissociation constant, ΔF is the change in free energy when a mole of undissociated acid in its standard state is replaced by an equivalent amount of its ions each in the hypothetical standard state. Then $RT \ln \frac{K^*}{K}$ (K^* and K being the ionization constants in mixed solvent and in water, respectively)

measures the change in free energy when a mole of undissociated acid is transferred from the mixed solvent to pure water and the ions are transferred in the opposite direction. Further, if we work on the mole fraction scale for the ionization constant, these transfers occur between states of the same mole fraction and there is no energy term corresponding to 'ideal gas expansion'. Moreover, the transfers occur between states of unit activity coefficient; there is, therefore, no term to be introduced for interionic effects. The term RT $\log \frac{K^*}{K}$ should measure the effect of the solvent on the ions and undissociated molecules.

In order to relate the medium effects to the ionization constant of a weak acid, we will make use of a buffered cell (3, 33) of the type

$$Pt,H_2(1atm.)|HR(m_1),MR(m_2),MCl(m_3),\ \text{organic solvent}(X),H_2O(Y)|AgCl,Ag \qquad ....43$$

This is essentially a cell containing hydrogen ions derived from the weak acid HR, and chloride ions from MCl, together with two electrodes reversible to these ions. Although such cells are limited to the determination of ionization constants only, they are peculiarly well adapted for this purpose. Buffer action permits accurate and easy measurements of small hydrogen ion concentration at relatively low ionic strength. In this cell, the cation, M, is usually sodium or potassium, m_1, m_2, and m_3 are the molalities of the respective constituents. The medium is naturally a mixed solvent.

There are two equivalent ways of expressing the electromotive force of such a cell,

$$ {}^{s}E = {}^{s}E^{o} - \frac{RT}{F} \ln {}^{s}_{s}\gamma_{H^+} \, {}^{s}_{s}\gamma_{Cl^-} - \frac{RT}{F} \ln m_{H^+} \, m_{Cl^-} \qquad \ldots.44 $$

and

$$ {}^{s}E = {}^{w}E^{o} - \frac{RT}{F} \ln {}^{s}_{w}\gamma_{H^+} \, {}^{s}_{w}\gamma_{Cl^-} - \frac{RT}{F} \ln m_{H^+} \, m_{Cl^-} \qquad \ldots.45 $$

Here the superscripts and the subscripts have the same significance as expressed in equation (32), (33) and (35). It should be pointed out that the mean activity coefficient will no longer be used for the activity coefficient of hydrogen ion and chloride ion since in most cases, the actual molal concentration of the ions will not be the same as in the case of hydrochloric acid solution.

In equation (44), ${}^{s}E^{o}$ is the standard potential of the Ag-AgCl electrode in the mixed solvent, and ${}^{w}E^{o}$, in equation (45), is the standard potential of the electrode in pure water.

Equating equations (44) and (45), since they represent the same electromotive force, we get

$$ {}^{s}E^{o} - \frac{RT}{F} \ln {}^{s}_{s}\gamma_{H^+} \, {}^{s}_{s}\gamma_{Cl^-} - \frac{RT}{F} \ln m_{H^+} \, m_{Cl^-} = {}^{w}E^{o} - \frac{RT}{F} \ln {}^{s}_{w}\gamma_{H^+} \, {}^{s}_{w}\gamma_{Cl^-} - \frac{RT}{F} \ln m_{H^+} \, m_{Cl^-} $$

This, on rearrangement, yields,

$$ ({}^{w}E^{o} - {}^{s}E^{o}) = \frac{RT}{F} \left[\ln {}^{s}_{w}\gamma_{H^+} \, {}^{s}_{w}\gamma_{Cl^-} - \ln {}^{s}_{s}\gamma_{H^+} \, {}^{s}_{s}\gamma_{Cl^-} \right] $$

$$ = \frac{RT}{F} \ln \frac{{}^{s}_{w}\gamma_{H^+} \; {}^{s}_{w}\gamma_{Cl^-}}{{}^{s}_{s}\gamma_{H^+} \; {}^{s}_{s}\gamma_{Cl^-}} \qquad \ldots.46 $$

To make use of the terms such as ${}^{s}E^{o}$, ${}^{w}E^{o}$, ${}^{s}_{s}\gamma$, ${}^{s}_{w}\gamma$, ${}^{s}_{w}\gamma_{o}$ etc. without confusion, we must be able to identify the reference state of any activity coefficient. For all concentrations, the activity coefficient of the electrolyte (HCl) can be written as:

$$\ln {}^{s}_{w}\gamma_{HCl} = \ln {}^{s}_{w}\gamma^{o}_{HCl} + \ln {}^{s}_{s}\gamma_{HCl} \qquad \ldots.47$$

Here ${}^{s}_{w}\gamma$ = activity coefficient of an electrolyte at a finite concentration in a mixed solvent referred to unity at infinite dilution in pure water.

${}^{s}_{w}\gamma_{o}$ = activity coefficient of an electrolyte at zero concentration in a mixed solvent referred to unity at infinite dilution in the aqueous state.

${}^{s}_{s}\gamma$ = activity coefficient of an electrolyte at a finite concentration in mixed solvent referred to unity at infinite dilution in the mixed solvent.

In equation (47), the term γ_{HCl} actually refers to the mean activity coefficient and is designated as $\gamma_{\pm}$. Now, if we add the quantity $-\ln {}^{w}_{w}\gamma_{\pm}$ to both sides of the equation (47), we get,

$$\ln \frac{{}^{s}_{w}\gamma_{\pm}}{{}^{w}_{w}\gamma_{\pm}} = \ln {}^{s}_{w}\gamma_{\pm o} + \ln \frac{{}^{s}_{s}\gamma_{\pm}}{{}^{w}_{w}\gamma_{\pm}} \qquad \ldots.48$$

Equation (48) gives the definitional relationship between the total, primary and secondary medium effects, with respect to first, second and third term of the equation.

Comparison of equation (48) with (42) shows that equation (47) is valid. If the activity coefficient of hydrochloric acid is

written as

$$\gamma_{HCl} = (\gamma_{H^+}\ \gamma_{Cl^-})^{\frac{1}{2}} \qquad \ldots.49$$

then equation (47) becomes,

$$\ln {}^{s}_{w}\gamma_{o\ HCl} = \ln \frac{{}^{s}_{w}\gamma_{HCl}}{{}^{s}_{s}\gamma_{HCl}}$$

or

$$\ln {}^{s}_{w}\gamma_{o\ HCl} = \tfrac{1}{2} \ln \frac{{}^{s}_{w}\gamma_{H^+}\ {}^{s}_{w}\gamma_{Cl^-}}{{}^{s}_{s}\gamma_{H^+}\ {}^{s}_{s}\gamma_{Cl^-}} \qquad \ldots.50$$

Now from equation (46), after proper rearrangement, we get

$$\tfrac{1}{2} \ln \frac{{}^{s}_{w}\gamma_{H^+}\ {}^{s}_{w}\gamma_{Cl^-}}{{}^{s}_{s}\gamma_{H^+}\ {}^{s}_{s}\gamma_{Cl^-}} = \frac{F({}^{w}E^{o} - {}^{s}E^{o})}{2RT} \qquad \ldots.51$$

Equating the equation (50) and (51)

$$\ln {}^{s}_{w}\gamma_{o\ HCl} = \tfrac{1}{2} \ln \frac{{}^{s}_{w}\gamma_{H^+}\ {}^{s}_{w}\gamma_{Cl^-}}{{}^{s}_{s}\gamma_{H^+}\ {}^{s}_{s}\gamma_{Cl^-}} = \frac{F({}^{w}E^{o} - {}^{s}E^{o})}{2RT}$$

or

$$\log {}^{s}_{w}\gamma_{o\ HCl} = \tfrac{1}{2} \log \frac{{}^{s}_{w}\gamma_{H^+}\ {}^{s}_{w}\gamma_{Cl^-}}{{}^{s}_{s}\gamma_{H^+}\ {}^{s}_{s}\gamma_{Cl^-}} = \frac{F({}^{w}E^{o} - {}^{s}E^{o})}{4.606\ RT} \qquad \ldots.52$$

Equation (52) shows that the primary medium effect of the organic solvent upon the activity coefficient of the hydrogen and chloride ion is directly proportional to the two standard state potentials.

The primary medium effect of the organic solvent upon the ionization constant of the acid can be determined by considering a cell

of the following type,

$$Pt,H_2(1\ atm.)|HR(m_1),\ MR\ (m_2),\ MCl\ (m_3)|AgCl\text{-}Ag \qquad \ldots.53$$

Let K_A is the thermodynamic ionization constant of the acid in pure water and be expressed by the law of mass action as

$$K_A = \frac{{}^{w}\gamma_{H^+}\ {}^{w}\gamma_{R^-}}{{}^{w}\gamma_{HR}} \cdot \frac{m_{H^+}\ m_{R^-}}{m_{HR}} \qquad \ldots.54$$

For a different solvent other than water, K_A^*, the thermodynamic ionization constant is a function of the medium and is represented by

$$K_A^* = \frac{{}^{s}\gamma_{H^+}\ {}^{s}\gamma_{Cl^-}}{{}^{s}\gamma_{HR}} \cdot \frac{m_{H^+}\ m_{R^-}}{m_{HR}} \qquad \ldots.55$$

In order to find out the relation between K_A (the thermodynamic ionization constant in pure water) and K_A^* (the thermodynamic ionization constant in mixed solvent), equation(48) is written in the following form:

$$\ln {}^{s}_{w}\gamma_{\pm} = \ln {}^{s}_{w}\gamma_{\pm o} + \ln {}^{s}_{s}\gamma_{\pm}$$

or

$${}^{s}_{w}\gamma_{\pm} = {}^{s}_{w}\gamma_{\pm o}\ {}^{s}_{s}\gamma_{\pm} \qquad \ldots.48A$$

Now K_A and K_A^* is related by the following definitional equation, the activity coefficient of which can be calculated from equation (48A),

$$K_A = {}^{s}_{w}\gamma^{2}_{A}\ k_A = {}^{s}_{w}\gamma^{2}_{oA}\ {}^{s}_{s}\gamma^{2}_{A}\ k_A = {}^{s}_{w}\gamma^{2}_{oA}\ K_A^* \qquad \ldots.56$$

in which

$$ {}^{s}_{w}\gamma^{2}_{A} = \frac{{}^{s}_{w}\gamma_{H^+} \; {}^{s}_{w}\gamma_{R^-}}{{}^{s}_{s}\gamma_{HR}} \; ; \quad {}^{s}_{w}\gamma^{2}_{oA} = \frac{{}^{s}_{w}\gamma_{oH^+} \; {}^{s}_{w}\gamma_{oR^-}}{{}^{s}_{w}\gamma_{o\,HR}} \; ; $$

$$ {}^{s}_{s}\gamma^{2}_{A} = \frac{{}^{s}_{s}\gamma_{H^+} \; {}^{s}_{s}\gamma_{R^-}}{{}^{s}_{s}\gamma_{HR}} \; ; \quad k_A = \frac{m_{H^+} \; m_{R^-}}{m_{HR}} $$

After appropriate substitution of the value of ${}^{s}_{w}\gamma^{2}_{oA}$ in equation (56, one obtains,

$$ K_A = \frac{{}^{s}_{w}\gamma_{oH^+} \; {}^{s}_{w}\gamma_{oR^-}}{{}^{s}_{w}\gamma_{oHR}} \cdot K_A^{*} \qquad \ldots.57 $$

It is worthwhile to mention in this connection that in equation (56), the values of k_A are different in different solvents. From equation (57), it is apparent that the thermodynamic ionization constant of a weak acid in one solvent can be calculated knowing the value in another solvent (usually water).

Equation (56) evidently points out that the primary medium effect upon each of the species involved in this equation must be known. A part of our research program was to study the primary medium effect of the organic solvent upon the ionization constant of the hydrochloric acid in a given mixed solvent.

<u>The Computation of the Relative Partial Molal Heat Content and the Relative Partial Molal Heat Capacity of Electrolytes (HCl acid) in Mixed Solvent From Electromotive Force:</u>

A relative partial molal property may be defined as the difference between the partial molal property in a given solution and its value in the reference state.

The relative free energy of one mole of solution is defined in the following way such that

$$F - F^{o} = N_1(\bar{F}_1 - \bar{F}_1^{o}) + N_2(\bar{F}_2 - \bar{F}_2^{o} + \ldots \quad \ldots.58$$

in which N_1, N_2 are the mole fractions of components one, two, respectively, $\bar{F}$ is the partial molal free energy of the component and $\bar{F}^{o}$ represents the partial molal free energy in the standard state.

Similarly, the relative heat content per mole of solution can be written as

$$H - H^{o} = N_1(\bar{H}_1 - \bar{H}_1^{o}) + N_2(\bar{H}_2 - \bar{H}_2^{o}) + \ldots. \quad \ldots.59$$

in which $\bar{H}$ represents the partial molal heat content of the component, and $\bar{H}^{o}$ represents that of the standard state.

By definition;

$$\bar{F}_i = \bar{F}_i^{o} + RT \ln a_i \quad \ldots.60$$

Equation (58) can now be expressed as

$$F - \bar{F}^{o} = N_1RT \ln a_1 + N_2RT \ln a_2 + \ldots. \quad \ldots.61$$

Making use of the standard thermodynamic relation,

$$\left[\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T}\right]_p = -\frac{\Delta H}{T^2} \quad \ldots.62$$

and $\Delta F = F - \bar{F}^{o}$; one obtains;

$$\left[\frac{\partial(N_1R \ln a_1 + N_2R \ln a_2 + \ldots.)}{\partial T}\right]_p = -\frac{\Delta H}{T^2} \qquad \ldots.63$$

Substitution of ΔH in equation (63) from equation (59), yields,

$$\left[\frac{\partial(N_1 \ln a_1 + N_2 \ln a_2 + \ldots.)}{\partial T}\right]_p = -\frac{N_1(\bar{H}_1 - \bar{H}_1^o) + N_2(\bar{H}_2 - \bar{H}_2^o) + \ldots.}{RT^2} \qquad \ldots.64$$

Instead of using the above general equation, it is customary to limit the investigation to each component separately. Thus,

$$\left[\frac{\partial \ln a_i}{\partial T}\right]_p = -\left[\frac{\bar{H}_i - \bar{H}_i^o}{RT^2}\right] \qquad \ldots.65$$

The relative partial molal heat content of the component i, $(\bar{H}_i - \bar{H}_i^o)$ is represented by $\bar{L}_i$, according to

$$\bar{L}_i \equiv \bar{H}_i - \bar{H}_i^o \qquad \ldots.65A$$

Differentiation of this equation with respect to temperature at constant pressure serves to define the important quantity, the partial molal heat capacity, $\bar{C}p_i$, and relative partial molal heat capacity $\bar{C}p_i - \bar{C}p_i^o$ at constant pressure. Hence,

$$\left[\frac{\partial \bar{H}_i}{\partial T}\right]_p - \left[\frac{\partial \bar{H}_i^o}{\partial T}\right]_p = \bar{C}p_i - \bar{C}p_i^o = \left[\frac{\partial \bar{L}_i}{\partial T}\right]_p = \bar{J}_i \qquad \ldots.65B$$

Now we return to equation (65), which can be re-written, after

substituting the value of $\bar{L}_2 = \bar{H}_2 - \bar{H}_2^o$, for one mole of electrolyte at a given temperature, as

$$\bar{L}_2 = \bar{H}_2 - \bar{H}_2^o = -RT^2 \left[\frac{\partial \ln a_2}{\partial T}\right]_p \quad \ldots.65C$$

in which a_2 = activity of an electrolyte in solution. Furthermore,

$$a_2 = a_+ \cdot a_-$$

or

$$a_2 = (m_+)^{\nu_+} \gamma_+^{\nu_+} (m_-)^{\nu_-} \gamma_-^{\nu_-}$$

or

$$a_2 = (m_\pm)^{\nu} \gamma_\pm^{\nu} \quad \ldots.65D$$

Equation (65C) is now expressed as,

$$\bar{L}_2 = \bar{H}_2 - \bar{H}_2^o = -RT^2 \left[\frac{\partial \ln (\gamma_\pm m_\pm)^{\nu}}{\partial T}\right]_p$$

and if m is kept constant,

$$\bar{L}_2 = -\nu RT^2 \left[\frac{\partial \ln \gamma_\pm}{\partial T}\right]_{p,m} \quad \ldots.65E$$

Partial molal heat contents are usually expressed relative to infinite dilution when they are called relative partial molal heat content. The mole fraction scale may be used to express the activity coefficient in equation (65E) but the molar scale is unsuitable since the composition of a solution of fixed molarity varies with the temperature.

The more general form of equation (65E) is

$$\left[\frac{\partial \ln \gamma_{\pm}}{\partial T}\right]_{p,m} = - \frac{\bar{L}_2}{\nu RT^2} \qquad \ldots.66$$

Now let us find out the relationship between the relative partial molal quantity, $\bar{L}_2$ and the electromotive force of the cell for an electrolyte in the mixed solvent. This can be done in the following way. From equation (33), the e.m.f. of the cell can be written in a more familiar form as

$$^{s}E = {}^{s}E^{o}_{m} - \frac{\nu RT}{NF} \ln \gamma_{\pm} m_{\pm}$$

or

$$\ln \gamma_{\pm} = - \frac{(^{s}E - E^{o}_{m})\, NF}{\nu RT} - \ln m_{\pm} \qquad \ldots.67$$

At constant composition m, the above equation is expressed as

$$\left[\frac{\partial \ln \gamma_{\pm}}{\partial T}\right]_{m} = - \frac{\partial}{\partial T} \left[\frac{(^{s}E - {}^{s}E^{o}_{m})\, NF}{\nu RT}\right] \qquad \ldots.68$$

If we equate the two equations, (66) and (68), we get,

$$\frac{\partial}{\partial T} \left[\frac{(^{s}E - {}^{s}E^{o}_{m})\, NF}{\nu RT}\right] = \frac{\bar{L}_2}{\nu RT^2} \; ;$$

or

$$\frac{\partial}{\partial T} \left[\frac{(^{s}E - {}^{s}E^{o}_{m})\, NF}{T}\right] = \frac{\bar{L}_2}{T^2}$$

or

$$\bar{L}_2 = NFT^2 \frac{\partial}{\partial T} \left[\frac{({}^sE - {}^sE^o_m)}{T} \right] \quad \ldots.69$$

Equation (69) is the well-known Gibbs-Helmholtz equation. Carrying out the differentiation, one obtains;

$$\bar{L}_2 = NFT^2 \left[({}^sE - {}^sE^o_m)\left(-\frac{1}{T^2}\right) + \frac{1}{T} \frac{\partial}{\partial T} ({}^sE - {}^sE^o_m) \right]$$

or

$$\bar{L}_2 = -NF ({}^s\bar{E} - {}^sE^o_m) + NFT \frac{\partial}{\partial T} ({}^s\bar{E} - {}^sE^o_m) \quad \ldots.70$$

Equation (70) shows that the determination of $\bar{L}_2$ from electromotive force measurements depends on the accuracy with which the temperature coefficient of the electromotive force can be determined.

The relative partial molal heat capacity may be computed from these relations, since

$$\bar{J}_2 \equiv \bar{C}_{p_2} - \bar{C}^o_{p_2} = \frac{\partial}{\partial T} (\bar{L}_2)_p \quad \ldots.71$$

Substituting the value of $\bar{L}_2$ from equation (70) and after proper differentiation one obtains,

$$\bar{J}_2 = \frac{\partial}{\partial T} -NF({}^sE - {}^sE^o_m) + NFT \frac{\partial}{\partial T} ({}^s\bar{E} - {}^sE^o_m)$$

or

$$\bar{J}_2 = -\frac{\partial}{\partial T} NF({}^sE - {}^sE^o_m) + NF \frac{\partial}{\partial T} ({}^sE - {}^sE^o_m) + NFT \frac{\partial^2}{\partial T^2} ({}^sE - {}^sE^o_m)$$

or

$$\bar{J}_2 = NFT \frac{\partial^2}{\partial T^2} ({}^sE - {}^sE^o_m) \quad \ldots.72$$

The most important question now arises about the right kind of function which can be employed for the computations of the variation

of $(\overset{s}{E} - {}^{s}E^{o}_{m})$ with respect to temperature. Although, it is known that $\bar{J}_2$ does not vary linearly with temperature, we shall assume as a first approximation that it does vary linearly, so that

$$\bar{J}_2 = \bar{J}_2(o) + c''' (T - T_o) \qquad \ldots.73$$

in which $\bar{J}_2(o)$ refers to some reference temperature, T_o, and c''' is a constant. After proper rearrangement, if equation (73) is now integrated between the limits T and T_o, we obtain,

$$\int_{T_o}^{T} d\bar{L}_2 = \int_{T_o}^{T} \bar{J}_2 \, dT$$

when $T = T_o$, $\bar{L}_2 = \bar{L}_2(o)$

Hence, $\bar{L}_2 - \bar{L}_2(o) = \int_{T_o}^{T} \bar{J}_2 \, dT$

or

$$\bar{L}_2 = \bar{L}_2(o) + \int_{T_o}^{T} \bar{J}_2 \, dT \qquad \ldots.74$$

Substituting the value of $\bar{J}_2$ from equation (73) in equation (74), one obtains;

$$\bar{L}_2 = \bar{L}_2 (o) + \int_{T_o}^{T} \{\bar{J}_2 (o) + c''' (T - T_o)\} \, dT$$

or

$$\bar{L}_2 = \bar{L}_2 (o) + \int_{T_o}^{T} \bar{J}_2 (o) \, dT + \int_{T_o}^{T} c''' \, TdT - c''' \int_{T_o}^{T} T_o \, dT$$

or

$$\bar{L}_2 = \bar{L}_2(o) + \bar{J}_2(o)\,T - \bar{J}_2(o)\,T_o + \frac{c'''T^2}{2} - \frac{c'''T_o^2}{2} - c'''T_oT + c'''T_o^2$$

or

$$\bar{L}_2 = \bar{L}_2(o) - \bar{J}_2(o)\,T_o + \frac{c'''T_o^2}{2} + (\bar{J}_2(o) - c'''T_o)\,T + \frac{c'''}{2}\,T^2$$

or

$$\bar{L}_2 = a'' + b''T + c''T^2 \qquad \ldots.75$$

where $a'' = \bar{L}_2(o) - \bar{J}_2(o)\,T_o + \frac{c'''T_o^2}{2}$

$$b'' = \bar{J}_2(o) - c'''T_o$$

and $c'' = c'''/2.$

Substituting equation (75) into equation (69), one obtains,

$$\frac{\partial}{\partial T}\left[\frac{({}^sE - {}^sE_m^o)}{T}\right] = \frac{1}{NFT^2}\,(a'' + b''T + c''T^2)$$

or

$$\int d\,\frac{({}^sE - {}^sE_m^o)}{T} = \frac{1}{NF}\int\left(\frac{a''}{T^2} + \frac{b''}{T} + c''\right) dT$$

or

$$\frac{{}^sE - {}^sE_m^o}{T} = \frac{1}{NF}\left(-\frac{a''}{T} + I + b''\ln T + c''T\right)$$

or

$$({}^sE - {}^sE_m^o) = \frac{1}{NF}\,(-a'' + IT + b''T\ln T + c''T^2) \qquad \ldots.76$$

where I = integration constant.

If the accuracy of the electromotive force is greater than ±0.05 mv; and the temperature range is greater than 40°C, then ${}^{s}E$ and ${}^{s}E^{o}_{m}$ may be expressed, including higher powers of T, as

$${}^{s}E = a' + b'T + c'T^2 + d' T \ln T$$

and

$${}^{s}E^{o}_{m} = a'_o + b'_o T + c'_o T^2 + d'_o T \ln T$$

Also,

$$(E_s - {}^{s}E^{o}_{m}) = (a' - a'_o) + (b' - b'_o)T + (c' - c'_o)T^2 + (d' - d'_o) T \ln T \quad \ldots.77$$

However, in actual practice, it has been found that over limited range of temperature (0° to 35°C), both ${}^{s}E$ and ${}^{s}E^{o}_{m}$ may be expressed to within ±0.05 mv by the following quadratic equations.

$${}^{s}E = a + bT + cT^2 \quad \ldots.78$$

and

$${}^{s}E^{o}_{m} = a_o + b_o T + c_o T^2 \quad \ldots.79$$

Hence, it appears that for limited range of temperature, the use of the logarithmic term is not necessary. If $({}^{s}E - {}^{s}E^{o}_{m})$ is expressed by the following equation,

$$({}^{s}E - {}^{s}E^{o}_{m}) = (a - a_o) + (b - b_o)T + (c - c_o)T^2 \quad \ldots.80$$

then according to equation (70),

$$\tilde{L}_2 = -NF[(a - a_o) + (b - b_o)T + (c - c_o)T^2] + NFT[(b - b_o) + 2(c - c_o) T]$$

or

$$\tilde{L}_2 = -NF [(a - a_o) + (b - b_o)T + (c - c_o)T^2] + NF[(b - b_o)T + 2(c - c_o)T^2]$$

or

$$\bar{L}_2 = -NF\,[(a - a_o) - (c - c_o)T^2]$$

Since N = 1, for uni-univalent electrolyte,

$$\bar{L}_2 = -F[(a - a_o) - (c - c_o)T^2$$

or

$$\bar{L}_2 = -F(a - a_o) + F(c - c_o)T^2 \qquad \ldots.81$$

$\bar{L}_2$ can also be simplified as

$$\bar{L}_2 = \alpha + \beta T^2 \qquad \ldots.82$$

in which $\alpha = -F(a - a_o)$

and $\beta = F(c - c_o)$

The relative partial molal heat capacity, $\bar{J}_2$ can also be written from equation (72) as,

$$\bar{J}_2 = 2F\,(c - c_o)T \qquad \ldots.83$$

or

$$\bar{J}_2 = 2\beta T \qquad \ldots.84$$

The constants a, a_o, c, c_o, i.e., the coefficients of the equations (78) and (79) are easily determined by the method of least squares from the e.m.f. data at various temperatures.

In our actual calculations, we need to know the more accurate values of E^o which were obtained from equation (28) by extrapolation to zero concentration or more precisely to zero molality. But this simple procedure may cause some error because of non-linearity at the lowest concentrations. In order to make the extrapolations as accurate as possible, the curve fitting technique utilizing the

IBM 1620 Computer was used. The details of this technique will be given in Chapter III.

This program is based on the assumption that a set of experimental data can be best fitted to a polynomial of the following form,

$$y = A_0 + A_1x + A_2x^2 + A_3x^3 \ldots\ldots + A_{15}x^{15} \qquad \ldots.85$$

In our calculations and plots, the quantity, E', which is equal to $(E_{obs} + \frac{2RT}{F} \ln m)$ given in equation (28), was taken as the ordinate and $m^{\frac{1}{2}}$ was taken as the abscissa. Now employing equation (85) and assuming that E' can be expressed as,

$$E_{obs} + \frac{2RT}{F} \ln m = A_0 + A_1m^{\frac{1}{2}} + A_2m + A_3m^{\frac{3}{2}} \qquad \ldots.86$$

we can easily determine the value of the standard potential, E^o in the mixed solvent by putting m equal to zero in equation (28).

To give theoretical justification of the assumption given in equation (86), let us re-write the equation (28),

$$E + \frac{2RT}{F} \ln m = E^o - \frac{2RT}{F} \ln \gamma_{\pm} \qquad \ldots.28$$

It can be shown from the work of Gronwall, LaMer and Sandved that $\ln \gamma_{\pm}$ can be expressed by an empirical equation as,

$$\ln \gamma_{\pm} = A'm^{\frac{1}{2}} + B'm + c'm^{\frac{3}{2}} + \ldots.$$

If we substitute this series equation into equation (28), we will obtain an equation which is very similar to the empirical equation (86).

For dilute solutions, the thermodynamic expressions in terms of the logarithm of the mean activity coefficients have been derived in detail by Debye and Hückel (3, 5, 6). In their derivations, the

following assumptions were made.

(i) Strong electrolytes are completely dissociated into ions, hence observed deviations from ideal behavior are ascribed to electrical interactions between the ions.

(ii) The distance of the closest approach of two ions "a" is the same for all kinds of ions in the solution.

(iii) At the distance of the closest approach to an individual ion, the potential and field strength are the same as for a point charge, and also equal to the charge of the ion in question and placed at its center.

(iv) If the dielectric constant of the solution is assumed to be that of the pure solvent, Poisson's equation is satisfied by the potential of the reference ion.

(v) For the purpose of calculating the electrostatic potential of an individual ion, the charges on all the other ions may be replaced by a continuous charge distribution which fills the space outside the distance of closest approach, is spherically symmetrical, and of a density determined by Boltzmann's statistical law.

Based on the above assumptions Debye and Hückel finally derived the following differential equation which usually goes by the name of Poisson-Boltzmann equation:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_i}{dr}\right) = -\frac{4\pi\epsilon}{D}\sum_{j=1}^{s}\frac{Nn_jZ_j}{V}\exp\left(-\frac{Z_j e\psi_i}{kT}\right) \qquad \ldots.86A$$

where ψ_i represents the electrostatic potential due to an ion of the ith kind at a distance r from that ion, D is the dielectric constant

of the pure solvent, ϵ represents the unit electric charge, and $Z_j\epsilon$ represents the charge on the jth ion, N is Avogadro's number; k is the Boltzmann constant; V is the volume of the solution which contains n_o moles of solvent and n_i moles of the ion of the ith kind; and T represents the absolute temperature.

Applying the boundary conditions,

(i) when $r \to \infty$, $\psi_i \to 0$

(ii) $\frac{d\psi_i}{dr} = \frac{\epsilon Z_i}{D} \cdot \frac{1}{a_i^2}$ for $r = a_i$, i.e., the medium is uniform and continuous throughout.

Assuming complete dissociation, Debye and Hückel were able to derive a quantitative expression for activity coefficient of ions in dilute solutions. The principle underlying this calculation is that due to the existence of the oppositely charged ionic atmosphere around each ion, dilution of a solution involves work against the electrostatic attraction over the free energy of dilution of an ideal solution which is usually determined by the decrease in concentration. For fairly dilute solutions, the activity coefficients are invariably less than might be expected on the basis of its concentration. The difference between the actual and the ideal free energy change serves as a measure of the activity coefficient and the expression for this extra free energy due to Coulombic interactions can be derived in the following way. In calculating the activity coefficients and other thermodynamic properties of the solution, Debye and Hückel attributed all the deviations from the behavior of ideal solutions to the electric charges on the ions. Let us consider the following process:

(i) An ion is gradually discharged in an extremely dilute solution of the electrolyte.

(ii) The discharged ion is transferred to a more concentrated solution and,

(iii) The ion is gradually charged again.

Step (ii) involves the Gibbs-free energy change for an ideal solution. The changes in Gibbs-free energy in steps (i) and (iii) are equal to the electrical work done on the system. The amount of electrical energy can be expressed by the following equation,

$$\Delta F_{j(elec)} = \int_{o}^{Z_j \epsilon} \psi_i \, de_j \qquad \ldots.87$$

in which $Z_j \epsilon$ and e_j represent the charge on the jth ion.

The chemical potential or the free energy of 1 mole of reference ion can be written in the thermodynamic term, as

$$\bar{F} - \bar{F}^{o} = RT \ln a_{\pm}$$

or

$$\bar{F} - \bar{F}^{o} = RT \ln \gamma_{\pm} m_{\pm}$$

or

$$\bar{F} - \bar{F}^{o} = RT \ln m_{\pm} + RT \ln \gamma_{\pm} \qquad \ldots.88$$

The right side of the above equation suggests that the free energy compared with the standard state, be thought of in terms of an ideal contribution corresponding to RT ln $m_{\pm}$ and a non-ideal contribution corresponding to RT ln $\gamma_{\pm}$. Thus, one might write the free energy change in two parts,

$$\bar{F}_{ideal} - \bar{F}^{o} = RT \ln m_{\pm} \qquad \ldots.89$$

and

$$\Delta\bar{F}_{non\text{-}ideal} = RT \ln \gamma_{\pm} \qquad \ldots.90$$

so that $\bar{F} = \bar{F}_{ideal} + \bar{F}_{non\text{-}ideal}$.

It is the term for the non-ideal free energy contribution that measures the change in free energy of the reference ions as a result of the non-ideal effects. If the potential energy or the electrostatic potential, ψ_i, due to the ionic interaction can be related to a free-energy effect, this quantity can be identified by equation (90), i.e., with RT ln $\gamma_{\pm}$.

Now the problem of immediate interest is to find out the correct expression for ψ_i. Expanding the exponential term in equation (86A), and neglecting all terms beyond the first because for solvents of high dielectric constants, $Z_j\epsilon\psi_i \ll kT$, it follows that

$$\exp\left(-\frac{Z_j\epsilon\psi_i}{kT}\right) \cong 1 - \frac{Z_j\epsilon\psi_i}{kT} \qquad \ldots.91$$

The higher terms in the above expansion must be taken into consideration if we deal with a solvent of low dielectric constant, where Debye and Hückel's approximation is not valid.

Let us consider an electrolyte at a concentration of n molecules per c.c. which dissociates into two kinds of ions, then the summation term in equation (86A) can be written as

$$\sum_1^2 \frac{Nn_jZ_j\epsilon}{V} \exp\left(-\frac{Z_j\epsilon\psi_i}{kT}\right) = \frac{\nu_1 Nn\, Z_1\epsilon}{V} \exp\left(-\frac{Z_1\epsilon\psi_i}{kT}\right)$$

$$+ \frac{\nu_2 NnZ_2\epsilon}{V} \exp\left(-\frac{Z_2\epsilon\psi_i}{kT}\right) \qquad \ldots.92$$

where ν_1 and ν_2 have their own physical significance.

For symmetrical types of electrolytes, $Z_1\epsilon = -Z_2\epsilon$, i.e., $\nu_1Z_1\epsilon = -\nu_2Z_2\epsilon$, the equation (92) is now given by,

$$\sum_1^2 \frac{Nn_jZ_j\epsilon}{V} \exp\left(-\frac{Z_j\epsilon\psi_i}{kT}\right) = \frac{\nu_1 NnZ_1\epsilon}{V} \left[\exp\left(-\frac{Z_1\epsilon\psi_i}{kT}\right) - \exp\left(\frac{Z_1\epsilon\psi_i}{kT}\right)\right] \ldots.93$$

In equation (92), the expression in brackets is the negative of twice the hyperbolic sine of $(\frac{Z_1 e\psi_i}{kT})$, and hence the summation is written as:

$$-\frac{2\nu_1 NnZ_1\epsilon}{V}\left[\frac{Z_1 e\psi_i}{kT}+\frac{1}{3!}\left(\frac{Z_1 e\psi_i}{kT}\right)^3+\frac{1}{5!}\left(\frac{Z_1 e\psi_i}{kT}\right)^5+\ldots\right] \qquad \ldots.94$$

It becomes apparent that for symmetrical valence type electrolytes, we have previously neglected the effects of terms of the 3rd, 5th and higher odd-numbered orders. Furthermore, it is also apparent that for unsymmetrical electrolytes terms of the even as well as odd-numbered orders must be considered. Gronwall, LaMer and Sandved (16) have developed and solved the equation for symmetrical type of electrolytes, e.g., hydrochloric acid where ν_1 and Z_1 are both unity. Substitution of equation (94) into equation (86A) gives a differential equation which can be solved by the method given by Gronwall, LaMer and Sandved (16).

For electrolytes of symmetrical valence types, i.e., $Z_1 = Z_2$, the extended equation for the logarithm of the mean activity coefficient is expressed as

$$\ln \gamma_{\pm} = -\frac{(\epsilon Z)^2}{2DkT}\cdot\frac{K}{1+Ka}+\left[\frac{(\epsilon Z)^2}{DkTa}\right]^3\left[\frac{1}{2}X_3(Ka)-2Y_3(Ka)\right]$$
$$+\left[\frac{(\epsilon Z)^2}{DkTa}\right]^3\left[\frac{1}{2}X_5(Ka)-4Y_5(Ka)\right] \qquad \ldots.95$$

in which a is the effective diameter of the ions, and the quantity, K, possesses the dimensions of a reciprocal distance and $\frac{1}{K}$ is regarded as the equivalent radius of the ionic atmosphere, hence depends on the concentration and valencies of the ions. K^2 is given by the following expression,

$$K^2 = \frac{4\pi\epsilon^2\Sigma n_i Z_i^2}{DkT} \qquad \ldots.95A$$

in which n_j is the number of ions of the ith species per volume of

solution. The first term on the right hand side of the equation (95) is identical with the following Debye and Hückel first approximation equations:

$$\ln \gamma_{\pm} = - \frac{(\epsilon Z)^2}{2DkT} \cdot \frac{K}{1+Ka}$$

or

$$\log \gamma_{\pm} = - \frac{S_f \Gamma^{\frac{1}{2}}}{1 + A \Gamma^{\frac{1}{2}}}$$

in which $A \equiv \frac{aK}{\Gamma^{\frac{1}{2}}}$, other symbols are already defined in equations (29) and (30).

The next two terms in equation (95) represent the contribution of the third and fifth order terms. $X_3(Ka)$, $Y_3(Ka)$, $X_5(Ka)$ and $Y_5(Ka)$ are complicated series functions of Ka, the values of which have been determined by Gronwall, LaMer and Sandved (16).

The conditions for departure from the original theory of Debye and Hückel become obvious from the nature of the coefficients of the terms in brackets. Deviations are expected to be more for higher valence type electrolytes, for example 2-2, 3-3, etc., and also for the small values of a. Furthermore, the wide departure from the first approximation can be found for solvents of lower dielectric constants.

The coefficients of the terms in brackets from equation (95) are expressed systematically but very precisely from the work of Gronwall, LaMer and Sandved (16).

$$X_3 = - \frac{1}{6} \frac{x^2}{(1+x)^4} [1 - 4x\, e^{4x}\, E(4x)] \qquad \ldots.96$$

in which

$$X = Ka,\ E(x) = \int_x^\infty \frac{e^{-u}}{u}\,du;\ \text{and}\ E(dx) = \int_x^\infty \frac{e^{-\alpha u}}{u}\,du$$

$$Y_3 = -\frac{f_1(x) - e^{4x}\,E(4x)\,f_2(x)}{6(1+x)^4} \qquad \ldots.97$$

in which $f_1(x) = \sum_{n=2}^{\infty} a_n X^n$ and $f_2(x) = \sum_{n=3}^{\infty} b_n X^n$;

$$X_5 = \frac{x^5}{120(1+x)^6}\left[-\frac{1}{3x^3} + \frac{1}{x^2} + \frac{14}{x} - 24e^{6x}\,E(6x) - \frac{80}{1+x}\,e^{4x}E(4x)\right.$$

$$\left. - \frac{80(1-x)}{(1+x)}\,e^{8x}\,E(4x)^2 + 80\,e^{6x}\int_x^\infty \frac{e^{-2u}\,E(4u)\,du}{u}\right] \qquad \ldots.98$$

and also,

$$Y_5 = \frac{1}{120(1+x)^7}\left[f_1(x) + f_2(x)\,e^{4x}\,E(4x) + f_3(x)\,e^{8x}\,E(4x)^2\right.$$

$$\left. + f_4(x)\,e^{6x}\left\{\int_x^\infty \frac{e^{-2u}\,E(4u)du}{u} - \frac{3}{10}\,E(6x)\right\}\right] \qquad \ldots.99$$

in which $f_1)x) = \sum_{n=5}^{\infty} a_n x^n$, $f_2(x) = \sum_{n=5}^{\infty} b_n x^n$, $f_3(x) = \sum_{n=5}^{\infty} C_n x^n$, and

$f_4(x) = \sum_{n=5}^{\infty} d_n x^n$.

The fraction, $\frac{K}{1+Ka}$ in equation (95) can be expressed as,

$$\frac{K}{1+Ka} = K - K^2a + K^3a^2 - K^4a^3 + K^5a^4 \quad \ldots.100$$

and that the quantity, $\frac{(eZ)^2}{2DkT}$ is a constant under the usual conditions of the experiment at constant temperature.

Now let us consider some of the terms of X_3 given in equation (96), where E (4x) is represented by

$$E(4x) = \int_x^\infty \frac{e^{-4u}}{u}\, du \quad \ldots.101$$

The solution of the above integral is

$$E(4x) = \log \frac{1}{x} - C - \sum_{\nu=1}^{\infty} \frac{(-4)^\nu x^\nu}{\nu!\ \nu} \quad \ldots.102$$

in which $\log \frac{1}{x}$ is expressed in series form and C is Euler constant (16).

Also, e^{4x} in equation (96) can be expanded as follows:

$$e^{4x} = 1 + 4x + \frac{16x^3}{2!} + \frac{64x^3}{3!} + \ldots. \quad \ldots.103$$

Furthermore, the fraction, $\frac{x^2}{(1+x)^4}$ can be expressed as a series similar to that of equation (100).

Now the most important thing concerning equation (96) is that all the terms are expressed as a series or the product of some series, hence X_3 might be expressed as the combination of several series.

Equation (97), in turn, can also be expressed in a series in X since $f_1(x)$, $f_2(x)$, e^{4x} and $E(4x)$, etc., are series expansions.

Because of the mathematical complexity in expressing all the terms, given by equations (98) and (99) for X_5 and Y_5, in series, one

can easily express X_5 and Y_5 in series functions the same way as it is used in X_3 and Y_3.

By combining all these series functions, equation (95) may be expressed in a series in K; since X = Ka; equation (95) can be written in the following form:

$$\ln \gamma_{\pm} = A''K + B''K^2 + C''K^3 + D''K^4 + \ldots. \qquad \ldots.104$$

in which the constants A'', B'', etc., are determined by combining the various series concerned. We already know that K^2 is proportional to the number of moles of electrolyte per volume of solution and consequently to the number of moles of electrolyte per 1000 gms. of solvent, or molality m.

Equation (104) now becomes,

$$\ln \gamma_{\pm} = A'm^{\frac{1}{2}} + B'm + C'm^{\frac{3}{2}} \qquad \ldots.105$$

Substituting the value of $\ln \gamma_{\pm}$ from equation (105) into equation (28), one obtains

$$E + \frac{2RT}{F} \ln m = E^{o} - \frac{2RT}{F} [A' m^{\frac{1}{2}} + B'm + C'm^{\frac{3}{2}} + \ldots.]$$

or

$$E + \frac{2RT}{F} \ln m = E^{o} + A m^{\frac{1}{2}} + Bm + Cm^{\frac{3}{2}} + \ldots. \qquad \ldots.106$$

Equation (106) is similar to equation (86), implying thereby that the curve fitting technique with the computer yields an equation analogous to that obtained by using the higher terms of Debye-Hückel theory.

CHAPTER III

EXPERIMENTAL TECHNIQUES

The following cell was used in the thermodynamic studies of the mixed solvents.

$$Pt,H_2(1\ atm)|HCl(m),\ THF(X),\ Water(Y)|AgCl,Ag$$

Figure 1 shows the design of the cell. It consists of two hydrogen electrodes and two silver-silver chloride electrodes. Four readings of e.m.f. were taken by interchanging the pair of electrodes. The average e.m.f. data taken by means of Leeds and Northrup K-3 Universal type potentiometer, was used in our calculation. An Eppley standard cell having low temperature coefficient and a Rubicon galvanometer having a sensitivity of 0.004 μa/mm was used in conjunction with the potentiometer.

A Sargent water bath cooler and three Sargent thermonitor water baths were used to obtain the temperatures of 15°, 25° and 35°C. with a precision of ±0.01°C. But a 0°C bath was set up by using a styrofoam ice chest which contained the mixture of ice and water. The accuracy in the latter case is of the order of 0.5°C.

The hydrogen electrodes (1,10) were made from a Sargent half-cell platinum electrode having a length of approximately 12 cm and thickness of about 0.125 mm. To clean the electrodes, an acid solution was prepared by mixing three volumes of 12M HCl acid with one volume of 16M HNO_3 and four volumes of distilled water. The platinum electrodes were first immersed in this acid solution for a short time and then thoroughly washed with distilled water. Platinum black was then deposited on the clean platinum foil by electrolyzing the platinum electrode in a solution of chlorplatinic acid containing a little lead acetate. The finished electrodes were stored in water.

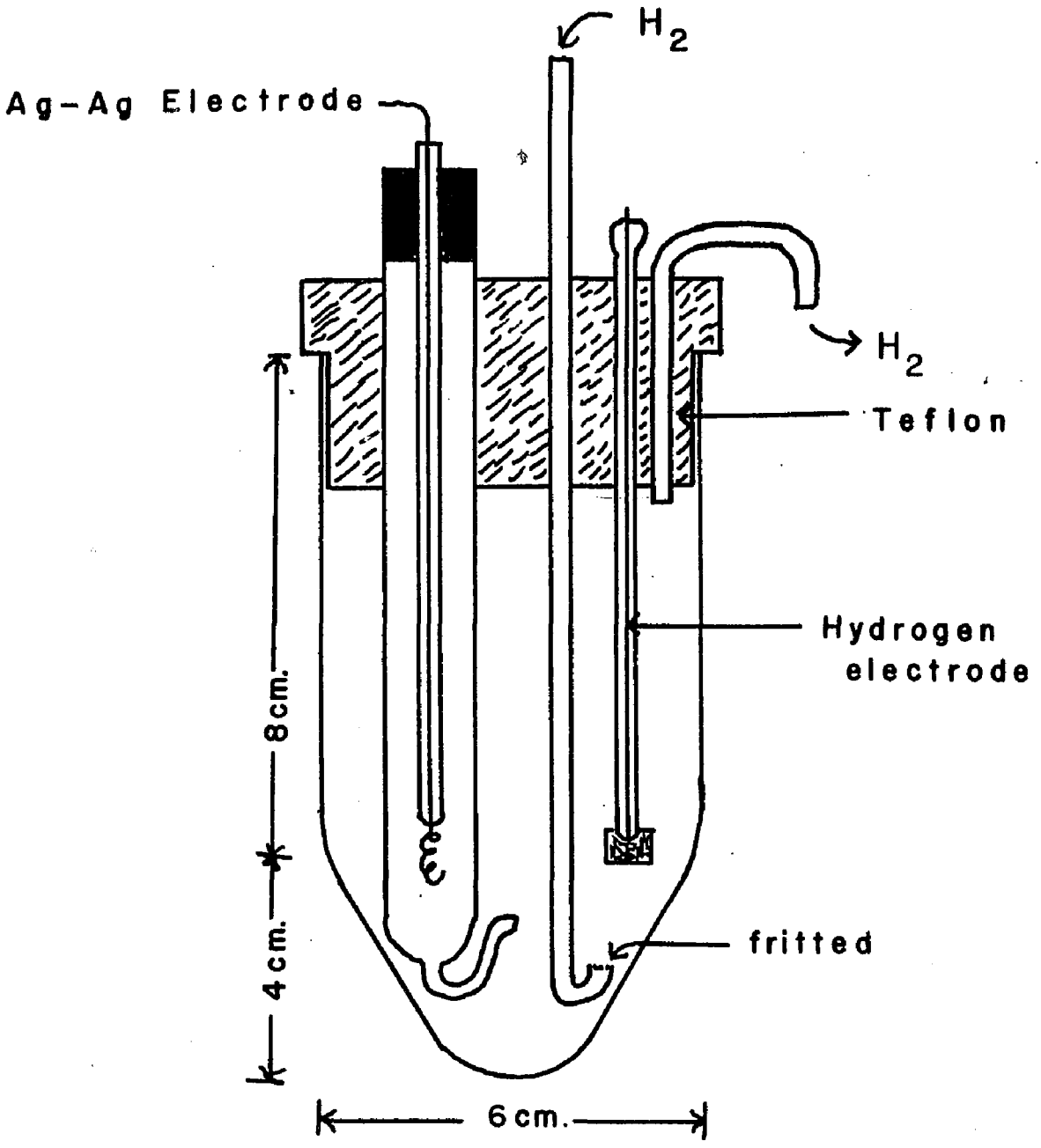
H2
Ag–Ag Electrode
H2
Teflon
Hydrogen
electrode
8cm.
4cm.
fritted
6cm.

FIGURE I

It is perhaps worthwhile to discuss in some detail the preparation of the platinizing solution since this solution is one of the important factors in the preparation of good hydrogen electrodes. The following procedure was found to be most satisfactory.

Preparation of Platinum Solution:

About 1 gm. of scrap platinum was cleaned in hot concentrated HNO_3 acid, rinsed with distilled water and ignited in a Bunsen flame. The platinum metal was cut into small fragments, and was digested in warm aqua-regia for dissolution. It took several days to complete this digestion. The acid platinum mixture was evaporated to dryness on a steam bath and then the residue was taken up with 20 ml of concentrated hydrochloric acid. By the repetitive procedure of evaporation and addition of concentrated hydrochloric acid, the residue, chloroplatinic acid hexahydrate, $H_2Pt\ Cl_6 \cdot 6H_2O$, was obtained after the fourth evaporation on the steam bath. This residue was then dissolved in 100 ml of distilled water followed by the addition of 80 milligrams of lead acetate trihydrate. The perfectly clear solution was stored in a glass stoppered bottle.

Platinization:

A current of 200 ma was passed for 1 to 3 minutes in such a direction that the electrode to be coated was the cathode and a similar platinum electrode was made the anode. When the same platinizing solution was used repeatedly, control of the current did not necessarily assure the production of the satisfactory electrodes, because the current efficiency decreased as the platinum was depleted. The conditions of plating are not critical, when the platinum solution is properly made.

Several finished electrodes were prepared as described above. The surface coat was uniform, very black and non-streaking. The presence of lead acetate had a marked effect on the character of the electrodeposited platinum, possibly through an increase of the grain size. In our work, it was found that the lighter coatings were better than heavy coatings. The lifetime of the electrodes was several months.

There were other types of hydrogen electrodes that were tried. These included a platinized electrode with a light gray coating, a platinum electrode which had no platinum black coating, and a suspension electrode according to Hills and Ives (10,30).

The potentials of the finished hydrogen electrodes were compared against each other and only those electrodes which agreed within ±0.1 millivolts were used.

Preparation of Ag-AgCl Electrodes:

The silver-silver chloride electrodes were prepared according to Bates (1).

Three common types of electrodes were usually recognized:

(i) the electrolytic type

(ii) the thermal-electrolytic type, and

(iii) the thermal type.

The author has used the convenient thermal electrolytic type which can be prepared in the following way according to Bates (1).

The base for each electrode was a helix of No. 26 platinum wire or silver wire of about 7 mm in length and 2 mm in diameter, sealed in a tube of flint glass. The bases were cleaned in warm 6M HNO_3 and then washed with distilled water. A thick paste of well-washed silver oxide

and water was applied to each helix. The electrodes were then suspended in a crucible furnace heated to a temperature of about 500°C until the paste turned white. To make the surface of each electrode smooth, the process was repeated using a slightly thinner paste for each additional coat.

Preparation of Silver Oxide:

About 338 gms. of $AgNO_3$ were dissolved in 3 liters of water. A solution of NaOH prepared by dissolving approximately 80 gms. of NaOH in 400 ml of water, was added dropwise to the vigorously stirred solution of $AgNO_3$. The silver-oxide precipitate formed was washed at least forty times and then was stored with distilled water in a glass stoppered bottle.

Electrolyzation:

The silver electrodes were then electrolyzed in a 1M HCl acid solution for 45 minutes at a current of 10 ma, using a platinum wire as cathode and the Ag electrode as anode. Because of its sluggishness, thick coats of AgCl must be avoided. The completed electrodes were placed in 0.05 M HCl acid solution overnight and then was stored in distilled water for use. The potentials of the electrodes were intercompared and the electrodes differing in potentials by more than 0.1 mv. were rejected. Four out of fourteen electrodes were good. The color of the electrodes was light gray. Two important points must be remembered in the preparation of silver-silver chloride electrodes:

(i) the purity of the hydrochloric acid,

(ii) the washing of the silver oxide.

An approximately 1N stock solution of hydrochloric acid was prepared

from reagent-grade acid by distilling twice in an all-glass still, each time only the middle fraction was kept. This stock solution was standardized volumetrically with Na_2CO_3, and gravimetrically, weighing as silver chloride. The methods of standardization have been discussed in detail in the reference (8). Distilled water used was obtained by redistilling once distilled water containing several crystals of permanganate with a few pellets of KOH. Distillation was made in an all-glass still with a column of glass beads about 18 inches long and $2\frac{1}{2}$ inches in diameter. The conductivity of the freshly prepared distilled water used in our work was less than 1×10^{-6} mho.

Purification of Tetrahydrofuran:

Tetrahydrofuran was purified by column chromatography (41). Commercially available tetrahydrofuran obtained from Fisher Scientific Company was purified by passing 100 to 200 ml THF through a column of (10 x 1.8 cm) containing 1 part of celite to 3 parts of freshly activated alumina in nitrogen atmosphere. The purified solvent was immediately stored over alumina and was then analyzed by gas chromatograph and refractometry. The boiling point of the pure solvent was 65.5°C at 748 mm, the refractive index and the density at 25°C was 1.40496 and 0.8829, respectively; these values correspond to the values given in literature.

Choice of the Solvent:

Tetrahydrofuran is a very powerful and versatile solvent. It is a good solvent for resinous as well as non-resinous materials; it dissolves rubbers, high molecular weight vinyl chlorides, copolymers, plastics whose uses have been seriously handicapped by the difficulty

of dissolving and getting them into solution. It is extremely useful in fabric coatings, film casting and in adhesives. It is miscible with water and almost in all organic solvents. In studying chemical equilibria, precipitation reaction, chelate formation, etc., tetrahydrofuran is used as the organic part in the mixed solvent.

Ten different solutions for each system, five in all, were prepared volumetrically by mixing the respective quantities of stock solution of hydrochloric acid, tetrahydrofuran and distilled water. The concentration of each solution was expressed in terms of molality ranging from 0.1 to 0.001 molal. Five different systems of the tetrahydrofuran-water mixture were studied at four different temperatures, 0°, 15°, 25° and 35°C. The composition of each system was then expressed as weight percent of the solvent; namely, 8.98, 18.21, 47.20 and 89.00.

The hydrogen gas used for this study was Matheson ultrapure hydrogen. The system attained the equilibrium in a short time with the use of a small frit (to ensure saturation of the call solution). The use of these adaptations enabled a steady state to be reached.

Experimental Technique:

The general procedure in obtaining the e.m.f. data was to put the cell containing the solution in the thermostatic bath, and then pass hydrogen gas through the cell solution until equilibrium was reached. It was assumed that the equilibrium was reached when the e.m.f. measurement taken over a period of half-hour agreed to within ±0.1 mv. It was found that the system reached in equilibrium a bit faster at higher temperature. The average time taken to reach equilibrium was two to three hours, less time was required at higher solvent composition.

The flow rate of the hydrogen gas was one of the criteria used to determine whether the system was at equilibrium or not. The e.m.f. readings were taken with and without by-passing the hydrogen gas. At equilibrium, this difference in e.m.f. data was negligible. Measurements of electromotive forces were rather difficult for low concentrations of hydrochloric acid and high concentrations of the organic solvent, since the galvanometer deflection was not large. The null point was detected easily for more concentrated hydrochloric acid solution.

The reproducibility of the potentiometric measurements of the galvanic cells depended on various factors, e.g., the composition of the mixed solvent. The higher the concentration of the organic solvent, the poorer was the reproducibility. To check the reproducibility, electromotive force measurements were first made at four different temperatures, and then were rechecked at the original temperature.

The reproducibility for solutions of 8.98 and 18.21 percent tetrahydrofuran was within ±0.1 mv. The e.m.f. data between the first reading and then when it was repeated for the second time agreed to almost ±0.2 to ±0.3 millivolt. As the percent composition of the solvent was increased, the reproducibility was more difficult especially at higher temperature. The explanation for not having good reproducibility might be due to the fact that the higher the solvent composition and the temperature, the greater the probability of losing the volatile solvent. Interesting evidence regarding this was the high e.m.f. data of the same cell solution at a particular higher temperature when it was repeated after passing the hydrogen gas for 12 hours. A careful observation of e.m.f. data from 5 different systems having almost the same

concentration of hydrochloric acid indicated the decrease in e.m.f. values as the percent of tetrahydrofuran was increased.

CHAPTER IV

EXPERIMENTAL DATA AND RESULTS

The primary medium effect was calculated with the use of logarithmic tables. However, the calculations of secondary medium effect, mean activity coefficients, relative partial molal heat capacity, relative partial molal heat content, etc. were carried out by means of the computer (IBM 1620) for five different systems (8.98, 18.21, 47.20, 73.03 and 89.00 weight percent of tetrahydrofuran), each system having ten different molalities of hydrochloric acid. The molalities of acid were calculated from appropriate density data of tetrahydrofuran (35) and that of water obtained from the Handbook of Chemistry and Physics. Table I represents the values of E_{obs} and E' obtained from the laboratory data with the first program in the computer

Equation (25) indicates the necessity of vapor pressure data of tetrahydrofuran and that of water in order to find out the proper correction factor which must be added to the laboratory electromotive force data to get $E_{observed}$ at one atmospheric pressure. For this reason, the barometric pressure was also recorded when each electromotive force was measured. According to different workers, there are other correction factors, for example, the depth of the hydrogen jet and vapor pressure lowering effect of hydrochloric acid upon the mixed solvent. These effects have been neglected in our studies in which the accuracy of the electromotive force measurements lies within tenth of millivolts. The vapor pressure data of water have been taken from Handbook of Chemistry and Physics; whereas, those of

tetrahydrofuran have been obtained from reference (15) at various temperatures and are given in Table II. The vapor pressure datum of tetrahydrufuran at 273.16°K has been computed by the method of least squares.

The polynomial curve fitting program was used in our extrapolations to obtain the most accurate values of the standard potential, E^{o} possible. The graphic extrapolations normally exhibit a high degree of error, especially when carried out along a curved portion of the plot.

It is worthwhile to discuss briefly the polynomial curve fitting technique. The revised version of the IBM 7.0.002 polynomial curve fitting program was used in our investigations. This program is based on the assumption that a set of experimental data can be fitted to a polynomial of the form:

$$Y = A_o + A_1x + A_2x^2 + ... A_{15}x^{15} \qquad ....85$$

The first approximation is the linear form, $Y = A_o + A_1x$. Of course, the first degree equation was not used in our studies because of slight curvature in the plots even at lower weight percent of tetrahydrofuran. The coefficients A_o, A_1, etc., are determined by the method of least square and the standard error of the dependent variable y is compared to a predetermined maximum tolerence. Higher order coefficients must be taken into consideration, if necessary, to have the error within the maximum tolerance. A modified Gaussian elimination technique was used to solve the resulting set of linear equations. The added advantage of this program is the optional use of

TABLE I

VALUES OF m, E_{obs} AND E′ OF HYDROCHLORIC ACID IN TETRAHYDROFURAN-WATER MIXTURES AT VARIOUS TEMPERATURES

X = weight percent of tetrahydrofuran

m = molality of hydrochloric acid

X = 8.98

	0°C		15°C		25°C		35°C	
m	E_{obs}	E′	E_{obs}	E′	E_{obs}	E′	E_{obs}	E′
0.11140	0.34454	0.24125	0.34199	0.23301	0.33585	0.22304	0.33352	0.21700
0.08905	0.35479	0.24096	0.35189	0.23181	0.34665	0.22240	0.34513	0.21671
0.07679	0.35995	0.23914	0.35706	0.22962	0.35395	0.22210	0.35223	0.21595
0.04449	0.38459	0.23809	0.38355	0.22901	0.38155	0.22165	0.38082	0.21555
0.03519	0.39538	0.23785	0.39464	0.22847	0.39351	0.22154	0.39276	0.21505
0.02111	0.41897	0.23739	0.41887	0.22731	0.41753	0.21931	0.41975	0.21490
0.01299	0.44143	0.23698	0.44140	0.22573	0.44100	0.21784	0.44445	0.21382
0.00779	0.46475	0.23628	0.46585	0.22482	0.46582	0.21643	0.46992	0.21215
0.00462	0.48911	0.23598	0.49115	0.22412	0.49170	0.21540	0.49756	0.21200
0.00231	0.52094	0.23519	0.52495	0.22350	0.51900	0.21420	0.53341	0.21105

TABLE I (Cont.)

X = 18.21

m	0°C		15°C		25°C		35°C	
	E_{obs}	E'	E_{obs}	E'	E_{obs}	E'	E_{obs}	E'
0.22588	0.30430	0.23428	0.30331	0.22945	0.29646	0.22003	0.29502	0.21603
0.11271	0.33769	0.23495	0.33744	0.22906	0.33162	0.21948	0.32932	0.21342
0.09940	0.34151	0.23285	0.34333	0.22871	0.33768	0.21908	0.33553	0.21295
0.09010	0.34511	0.23183	0.34612	0.22662	0.34252	0.21888	0.33992	0.21213
0.05960	0.36453	0.23080	0.37764	0.22480	0.36073	0.21585	0.36124	0.21150
0.04501	0.37655	0.22951	0.38753	0.22368	0.37410	0.21480	0.37478	0.21014
0.03560	0.38507	0.22809	0.36482	0.22193	0.38265	0.21130	0.38596	0.20887
0.01314	0.42894	0.22505	0.43374	0.21865	0.43240	0.20985	0.43211	0.20209
0.00467	0.47318	0.22060	0.48181	0.21536	0.48425	0.20855	0.48689	0.20195
0.00234	0.50377	0.21857	0.51343	0.21256	0.51822	0.20691	0.52338	0.21064

TABLE I (Cont.)

X = 47.20

m	0°C		15°C		25°C		35°C	
	E_{obs}	E'	E_{obs}	E'	E_{obs}	E'	E_{obs}	E'
0.23414	0.29279	0.22446	0.28645	0.21437	0.28024	0.20566	0.27097	0.19389
0.11679	0.32363	0.22256	0.31645	0.20983	0.31084	0.20052	0.30373	0.18971
0.09339	0.33281	0.22122	0.32704	0.20932	0.32050	0.19869	0.31553	0.18964
0.08052	0.33942	0.22085	0.33393	0.20885	0.32727	0.19785	0.32269	0.18893
0.04665	0.36132	0.21706	0.35669	0.20451	0.34621	0.21706	0.34745	0.18471
0.03690	0.37191	0.21661	0.36433	0.20511	0.35386	0.18435	0.36069	0.18095
0.01362	0.41371	0.21150	0.40799	0.19468	0.40122	0.18050	0.40492	0.17680
0.00817	0.43685	0.21060	0.43218	0.19350	0.42561	0.17865	0.42952	0.17428
0.00484	0.46028	0.20938	0.45686	0.19218	0.44986	0.17600	0.45587	0.17283
0.00242	0.49028	0.20676	0.48994	0.19085	0.48406	0.17460	0.48851	0.16866

TABLE I (Cont.)

X = 73.03

	0°C		15°C		25°C		35°C	
m	E_{obs}	E'	E_{obs}	E'	E_{obs}	E'	E_{obs}	E'
0.12050	0.29259	0.19300	0.27773	0.17266	0.26972	0.16100	0.26236	0.15000
0.09632	0.30214	0.19200	0.28818	0.17200	0.28023	0.16001	0.27325	0.14900
0.08305	0.30812	0.19101	0.29355	0.17001	0.28819	0.15400	0.27912	0.14700
0.04811	0.32682	0.18401	0.31564	0.16500	0.30709	0.15122	0.30010	0.13900
0.03806	0.33334	0.17950	0.32397	0.16168	0.31889	0.15097	0.30745	0.13390
0.02283	0.34995	0.17205	0.34239	0.15472	0.33654	0.14236	0.32569	0.12500
0.01404	0.36426	0.16350	0.35669	0.14490	0.35094	0.13180	0.34348	0.11700
0.00499	0.39945	0.15000	0.39515	0.13200	0.39127	0.11900	0.38241	0.10100
0.00250	0.42408	0.14201	0.42756	0.13000	0.42799	0.11100	0.41121	0.09300

TABLE I (Cont.)

X = 89.00

	0°C		15°C		25°C		35°C	
m	E_{obs}	E'	E_{obs}	E'	E_{obs}	E'	E_{obs}	E'
0.10823	0.23065	0.12600	0.21441	0.10401	0.21824	0.09110	0.19816	0.08010
0.09817	0.23425	0.12501	0.21835	0.10310	0.20924	0.09000	0.20234	0.07910
0.08464	0.24032	0.12410	0.22480	0.10220	0.21596	0.08910	0.20912	0.07801
0.04904	0.26101	0.11910	0.24681	0.09710	0.23758	0.08268	0.23159	0.07150
0.03879	0.27015	0.11720	0.25753	0.09618	0.24915	0.08220	0.24210	0.06955
0.02326	0.28784	0.11084	0.27168	0.08495	0.26825	0.07505	0.26178	0.06210
0.01432	0.30286	0.10300	0.28898	0.07815	0.28426	0.06610	0.27666	0.05220
0.00509	0.33352	0.08496	0.31790	0.05570	0.31399	0.04268	0.30369	0.02328
0.00254	0.35278	0.07161	0.33881	0.04220	0.33357	0.02666	0.32221	0.00501
0.00130	0.37556	0.06269	0.35919	0.02914	0.35419	0.01269	0.34169	0.01127

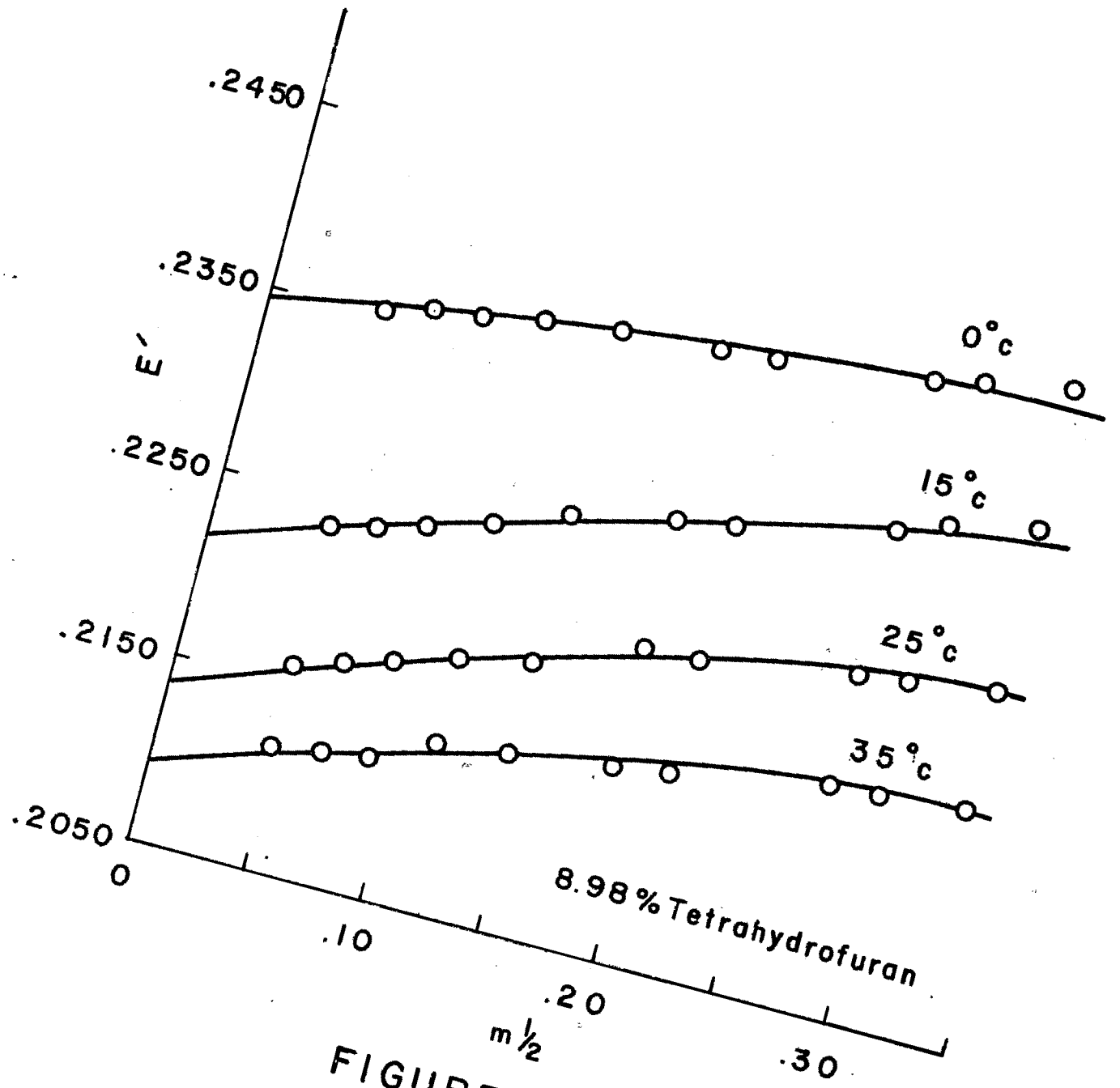
.2450
.2350
.2250
.2150
.2050
E'
0°c
15°c
25°c
35°c
0
.10
.20
.30
m½
8.98% Tetrahydrofuran

FIGURE 2

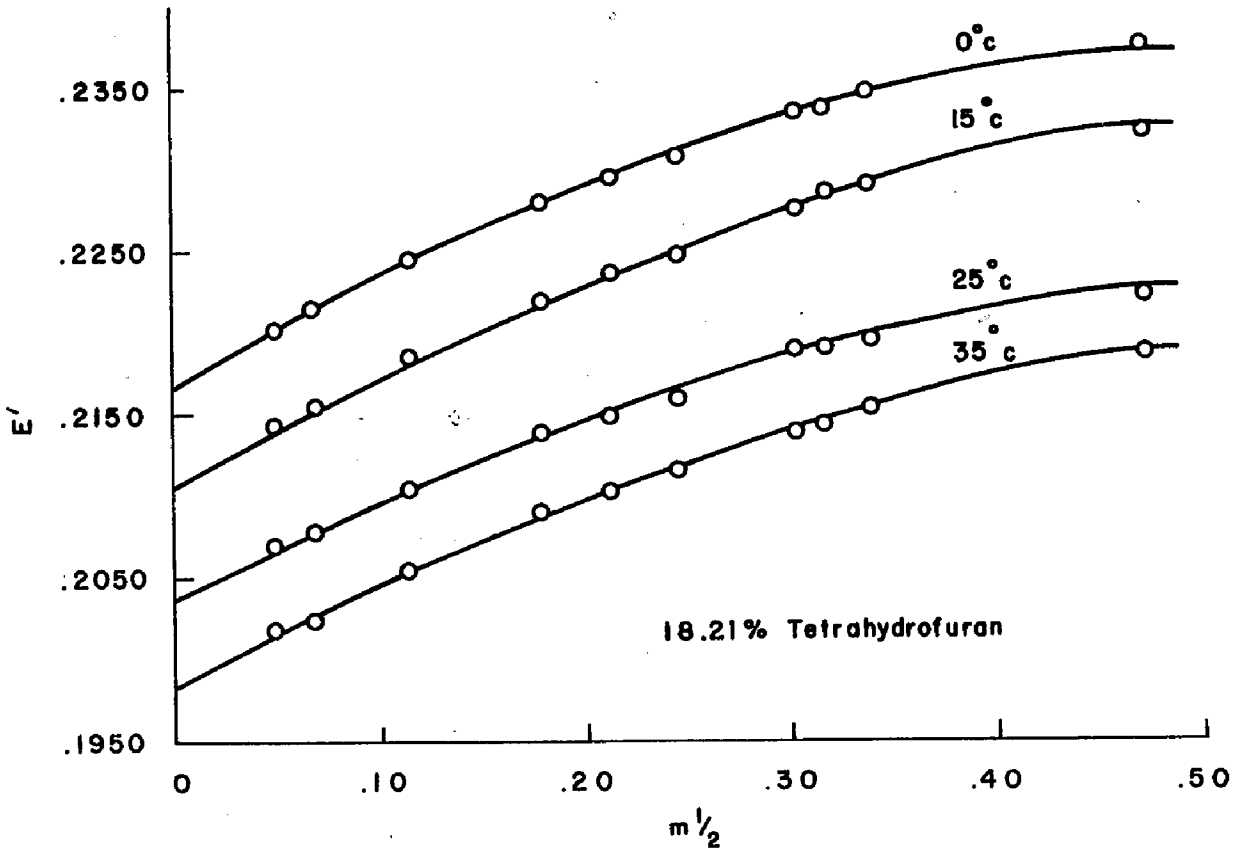
0°c
15°c
25°c
35°c
.2350
.2250
.2150
.2050
.1950
E'
18.21% Tetrahydrofuran
0
.10
.20
.30
.40
.50
m 1/2

FIGURE 3

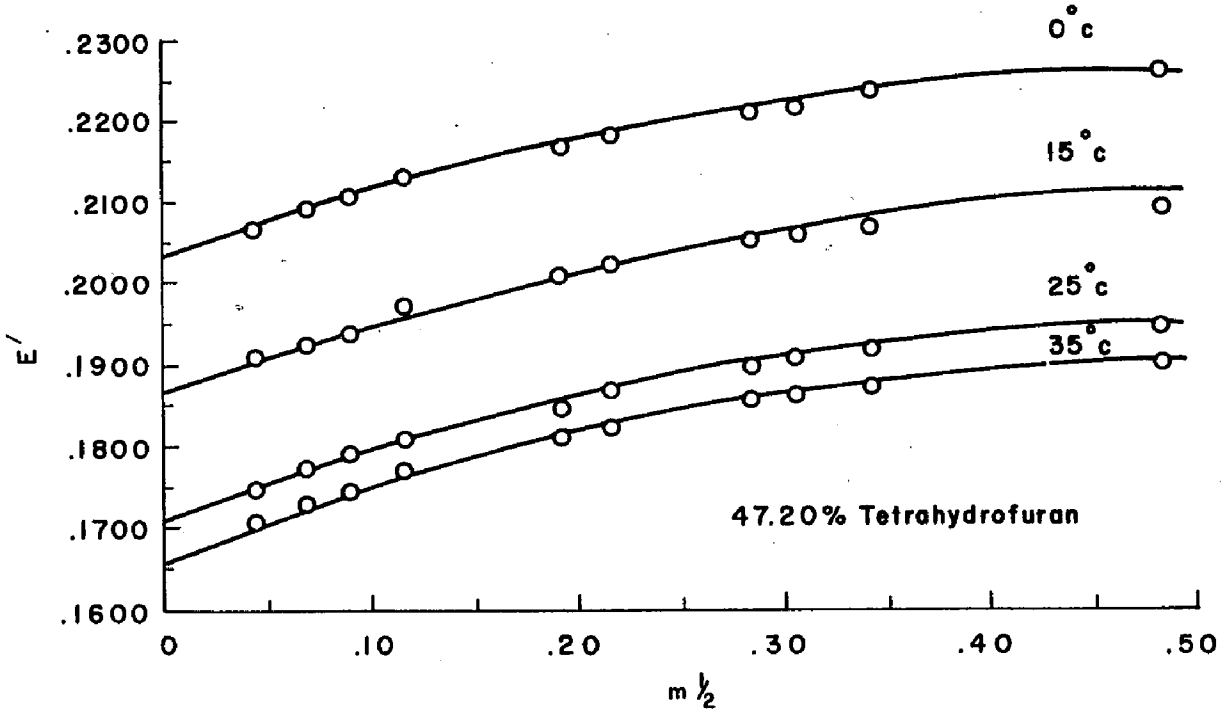
0°c
15°c
25°c
35°c
47.20% Tetrahydrofuran
E'
.2300
.2200
.2100
.2000
.1900
.1800
.1700
.1600
0
.10
.20
.30
.40
.50
m ½

FIGURE 4

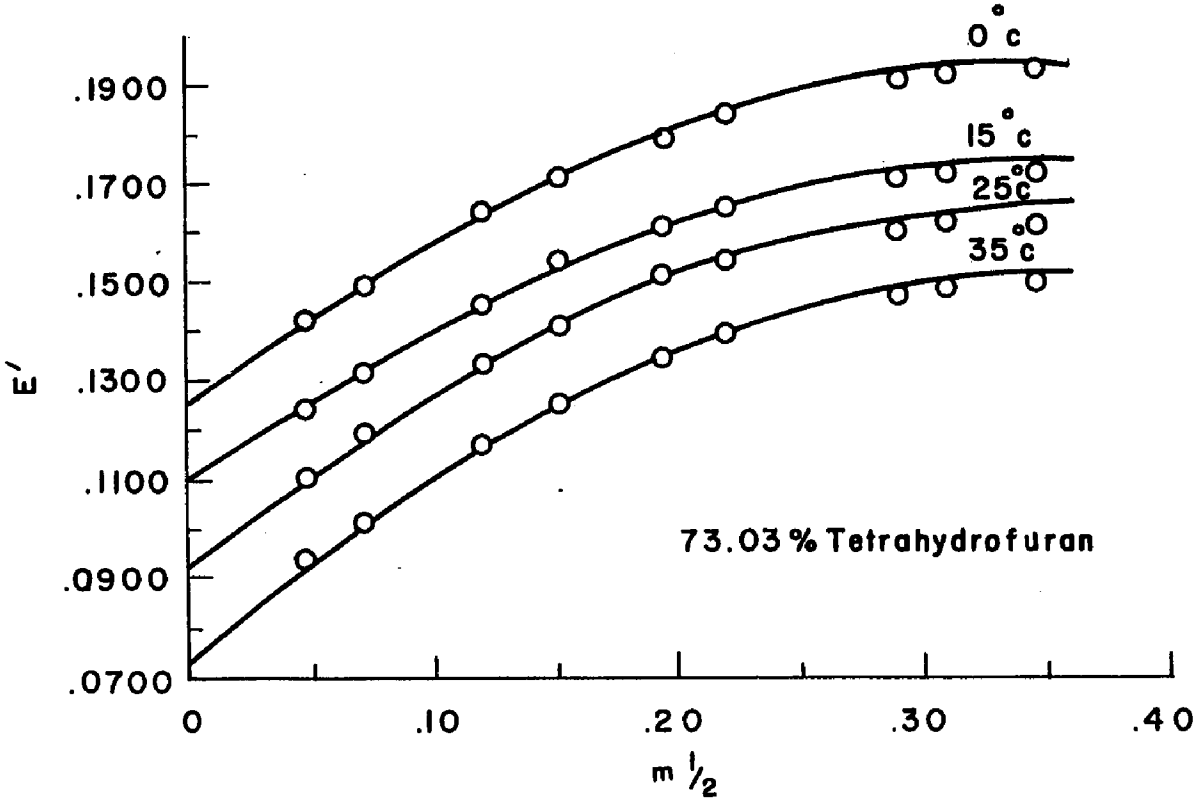
0°c
15°c
25°c
35°c
.1900
.1700
.1500
.1300
.1100
.0900
.0700
E'
0
.10
.20
.30
.40
m 1/2
73.03% Tetrahydrofuran

FIGURE 5

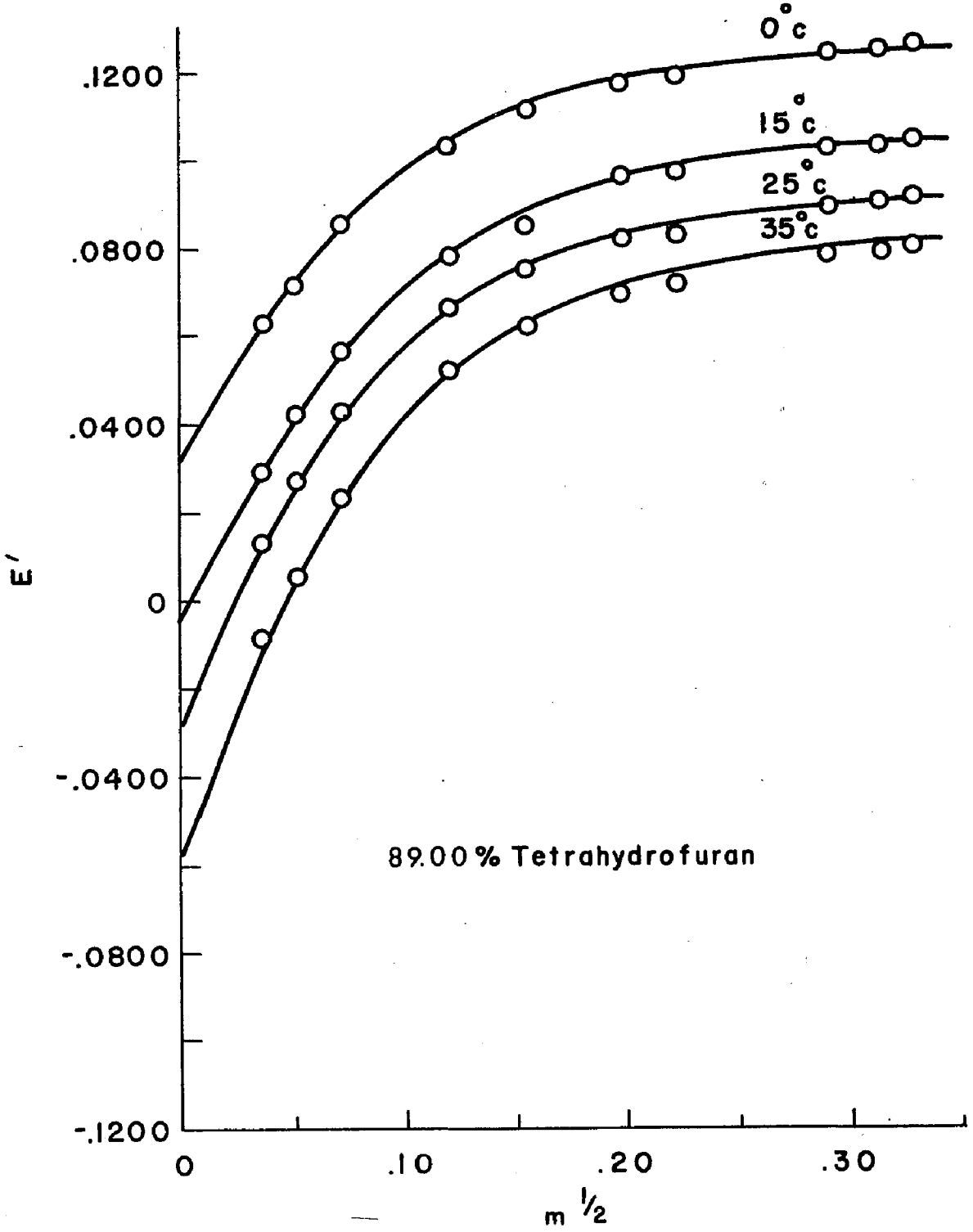
0°c
15°c
25°c
35°c
.1200
.0800
.0400
0
-.0400
-.0800
-.1200
E'
89.00% Tetrahydrofuran
0
.10
.20
.30
m 1/2

FIGURE 6

the weight factors. Furthermore, the highest degree coefficients can be obtained directly with or without designating the maximum tolerance.

Figures 2 through 6 contain plots of E', i.e., $E_{obs} + \frac{2RT}{F} \ln m$, a dependent variable as an ordinate against $m^{\frac{1}{2}}$, an independent variable as the abscissa of five different systems and at four different temperatures. The experimental points are represented by circles; whereas, the curves are the theoretical plots from polynomial curve fitting program (equation 85).

The question now arises as to the degree of equation to use in our extrapolations. The general nature of the curves drawn from experimental values and the standard error are the most useful criteria in deciding what degree equation to use in extrapolations.

In our investigations, no maximum tolerance was designated and the third degree equation was the highest polynomial fitted. The values of the coefficients of the empirical equation (85) and the standard error of each degree were calculated by the least squares method and are given in Table III for each system and temperature.

One of the main objects of our work was to determine the values of the standard potential, E^{o}, of the silver-silver chloride electrode in mixed solvents (tetrahydrofuran-water mixtures). These values of E^{o} were obtained by means of polynomial curve fitting program and are given in Table IV taken directly from the computer. Corrections within the limits of error of the experimental data are necessary for these values. However, no corrections were made until the final

quantities were obtained, since the values of E^o were used in all subsequent calculations. The limits of error and accuracy of the extrapolations will be discussed in Chapter V. The values of E^o for the aqueous system in Table IV have been taken from reference (3).

The mean activity coefficients of hydrochloric acid given in Table V are taken directly from the computer. The values for the aqueous system contain proper significant figures and have been obtained from reference (3); whereas, the values for the mean activity coefficients in the various mixed solvent systems corresponding to ${}^{s}_{s}\gamma_{\pm}$, were calculated from the following equation (107) obtained from equation (33), in which ${}^{s}E^{o}_{m}$ correspond to E^o values listed in Table IV

$$\ln \gamma_{\pm} = \frac{{}^{s}E^{o}_{m} - ({}^{s}E_{m} + \frac{2RT}{F} \ln m)}{\frac{2RT}{F}} \qquad \ldots.107$$

and ${}^{s}E_{m}$ correspond to E_{obs} given in Table I. The values of $(E_{obs} + \frac{2RT}{F} \ln m)$ at rounded concentrations were obtained from the following empirical equation which was used also for extrapolation purposes,

$$E_{obs} + \frac{2RT}{F} \ln m = A + Bm^{\frac{1}{2}} + Cm + Dm^{\frac{3}{2}} + \ldots. \qquad \ldots.108$$

the coefficients of which are given in Table III.

The primary medium effect ($\log {}^{s}_{w}\gamma_{o\pm}$ HCl) of tetrahydrofuran-water mixtures upon hydrochloric acid was calculated by means of the equation (37A) and are given in Table VI for each system at four

TABLE II

VAPOR PRESSURE DATA OF TETRAHYDROFURAN AND WATER

$t^{o}C$	Tetrahydrofuran	Water
0	84.8 mm	4.579 mm
15	114.0 mm	12.788 mm
25	176.0 mm	23.756 mm
35	263.0 mm	42.175 mm

TABLE IIA

DENSITY DATA OF TETRAHYDROFURAN AND WATER AT $25^{o}C$

Tetrahydrofuran (gm/ml)	Water (gm/ml)
0.8829	0.9970

TABLE III

THE COEFFICIENTS OF THE EMPIRICAL EQUATION,

$$E_{obs} + \frac{2RT}{F} \ln m = A + Bm^{1/2} + Cm + Dm^{3/2} + \ldots$$

FOR TETRAHYDROFURAN-WATER MIXTURES

X = weight percent of tetrahydrofuran

X = 8.98

t°C	A	B	C	D	Standard Error
0	0.23467	0.055295	-0.060449	0	0.000246
15	0.22160	0.060295	-0.056449	0	0.000191
25	0.21368	0.062295	-0.053448	0	0.000267
35	0.20933	0.065395	-0.053450	0	0.000283

X = 18.21

t°C	A	B	C	D	Standard Error
0	0.21662	0.056834	-0.054411	0	0.000227
15	0.21062	0.059832	-0.051412	0	0.000376
25	0.20375	0.062833	-0.047411	0	0.000306
35	0.19828	0.065864	-0.047667	0	0.000193

TABLE III(Cont.)

X = 47.20

$t^{\circ}C$	A	B	C	D	Standard Error
0	0.20365	0.082658	-0.075629	0	0.000520
15	0.18662	0.090563	-0.092187	0	0.000494
25	0.17060	0.095599	-0.113077	0	0.000403
35	0.16572	0.111072	-0.182976	0	0.000305

X = 73.03

$t^{\circ}C$	A	B	C	D	Standard Error
0	0.12600	0.353755	-0.592054	0	0.003224
15	0.11163	0.354590	-0.516553	0	0.001500
25	0.09310	0.407012	-0.624929	0	0.002459
35	0.07330	0.434337	-0.615825	0	0.000526

TABLE III(Cont.)

X = 89.00

$t^{\circ}C$	A	B	C	D	Standard Error
0	0.03397	0.916603	-3.355034	0.328130	0.000687
15	-0.00279	1.048794	-3.707654	0.591064	0.001346
25	-0.02582	1.265785	-4.968096	0.719111	0.001142
35	-0.05689	1.492791	-5.852357	0.880112	0.001220

TABLE IV

STANDARD POTENTIALS (E°) OF THE CELL,

H_2 (1 atm.)|HCl (m), THF (X), Water (Y)|AgCl, Ag

X and Y are weight percentages

X	0°C	15°C	25°C	35°C
0	0.23655	0.22857	0.22234	0.21565
8.98	0.23467	0.22160	0.21368	0.20933
18.21	0.21662	0.21062	0.20375	0.19828
47.20	0.20365	0.18662	0.17060	0.16572
73.03	0.12600	0.11163	0.09310	0.07330
89.00	0.03397	-0.00279	-0.02582	-0.05689

TABLE V

VALUES OF THE MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN TETRAHYDROFURAN-WATER MIXTURES AT VARIOUS TEMPERATURES

X = weight percent of tetrahydrofuran

X = 0

m	0°C	15°C	25°C	35°C
0.1	0.8027	0.8000	0.7964	0.7918
0.05	0.8346	0.8329	0.8304	0.8265
0.02	0.8774	0.8770	0.8755	0.8731
0.01	0.9065	0.9055	0.9048	0.9025
0.005	0.9303	0.9297	0.9285	0.9268
0.002	0.9541	0.9530	0.9521	0.9513
0.001	0.9668	0.9661	0.9656	0.9647
0.0005	0.9756	0.9757	0.9752	0.9745
0.0002	0.9848	0.9844	0.9842	0.9838
0.0001	0.9890	0.9890	0.9891	0.9886

X = 8.98

m	0°C	15°C	25°C	35°C
0.1	0.784	0.763	0.756	0.746
0.05	0.820	0.806	0.803	0.797
0.02	0.869	0.862	0.860	0.857
0.01	0.901	0.896	0.895	0.893
0.005	0.926	0.923	0.922	0.921
0.002	0.951	0.949	0.949	0.948
0.001	0.965	0.963	0.963	0.962
0.0005	0.975	0.974	0.973	0.973
0.0002	0.984	0.983	0.983	0.983
0.0001	0.988	0.988	0.988	0.988

TABLE V (Cont.)

X = 18.21

m	0°	15°	25°	35°
0.1	0.766	0.758	0.745	0.739
0.05	0.809	0.804	0.797	0.793
0.02	0.863	0.861	0.857	0.854
0.01	0.897	0.896	0.893	0.891
0.005	0.923	0.923	0.921	0.920
0.002	0.950	0.949	0.948	0.948
0.001	0.964	0.964	0.963	0.962
0.0005	0.974	0.974	0.973	0.973
0.0002	0.983	0.983	0.983	0.982
0.0001	0.988	0.988	0.987	0.987

X = 47.20

m	0°	15°	25°	35°
0.02	0.806	0.802	0.801	0.792
0.01	0.853	0.849	0.848	0.838
0.005	0.891	0.887	0.886	0.877
0.002	0.928	0.925	0.924	0.917
0.001	0.948	0.946	0.945	0.939
0.0005	0.963	0.961	0.960	0.956
0.0002	0.976	0.975	0.974	0.971
0.0001	0.984	0.982	0.981	0.979

TABLE V (Cont.)

X = 73.03

m	0°	15°	25°	35°
0.1	0.327	0.296	0.276	0.240
0.05	0.349	0.341	0.312	0.287
0.02	0.448	0.444	0.416	0.397
0.01	0.543	0.535	0.511	0.496
0.005	0.636	0.626	0.607	0.594
0.002	0.742	0.733	0.719	0.709
0.001	0.806	0.798	0.788	0.781
0.0005	0.857	0.851	0.843	0.838
0.0002	0.906	0.901	0.896	0.893
0.0001	0.932	0.929	0.925	0.923

X = 89.00

m	0°	15°	25°	35°
0.1	0.144	0.118	0.105	0.077
0.05	0.162	0.132	0.118	0.088
0.02	0.204	0.173	0.147	0.112
0.01	0.265	0.233	0.196	0.156
0.005	0.349	0.316	0.271	0.226
0.002	0.479	0.448	0.398	0.350
0.001	0.578	0.551	0.503	0.457
0.0005	0.670	0.647	0.604	0.563
0.0002	0.770	0.753	0.719	0.687
0.0001	0.829	0.816	0.789	0.763

TABLE VI

PRIMARY MEDIUM EFFECT ($\log {}^{s}_{w}\gamma_{\pm o}$ HCl) OF TETRAHYDROFURAN-WATER MIXTURES UPON HYDROCHLORIC ACID AT VARIOUS TEMPERATURES; COMPUTED FROM EQUATION (37A).

X = weight percent of tetrahydrofuran

x	0°	15°	25°	35°
8.98	0.0173	0.0609	0.0732	0.0517
18.21	0.1838	0.1569	0.1571	0.1420
47.20	0.3035	0.3668	0.4373	0.4083
73.03	1.0199	1.0227	1.0924	1.1641
89.00	1.8689	2.0233	2.0975	2.2289

TABLE VII

THE SECONDARY MEDIUM EFFECT OF TETRAHYDROFURAN-WATER MIXTURES UPON HYDROCHLORIC ACID AT VARIOUS TEMPERATURES. COMPUTED FROM EQUATION (42).

X = weight percent of tetrahydrofuran

	X = 8.98			
m	0°	15°	25°	35°
0.1	-0.010122	-0.020490	-0.022477	-0.025677
0.05	-0.007679	-0.013834	-0.014450	-0.015805
0.02	-0.004199	-0.007710	-0.007694	-0.008291
0.01	-0.002812	-0.004691	-0.004696	-0.004727
0.005	-0.001912	-0.003167	-0.002760	-0.002704
0.002	-0.001296	-0.001691	-0.001330	-0.001397
0.001	-0.000914	-0.001206	-0.000999	-0.000886
0.0005	-0.000402	-0.000862	-0.000643	-0.000532
0.0002	-0.000452	-0.000531	-0.000441	-0.000387
0.0001	-0.000243	-0.000421	-0.000461	-0.000327

	X = 18.21			
m	0°	15°	25°	35°
0.1	-0.020182	-0.023621	-0.029018	-0.029982
0.05	-0.013639	-0.015135	-0.018018	-0.018209
0.02	-0.007321	-0.008021	-0.009358	-0.009452
0.01	-0.004789	-0.004728	-0.005661	-0.005420
0.005	-0.003195	-0.003102	-0.003337	-0.003130
0.002	-0.002043	-0.001599	-0.001635	-0.001630
0.001	-0.001418	-0.001123	-0.001193	-0.001038
0.0005	-0.000747	-0.000794	-0.000770	-0.000633
0.0002	-0.000664	-0.000483	-0.000515	-0.000448
0.0001	-0.000390	-0.000385	-0.000512	-0.000369

TABLE VII (Cont.)

X = 47.20

m	0°	15°	25°	35°
.02	-0.036822	-0.038894	-0.038296	— 0.042339
.01	-0.026380	-0.028036	-0.028114	- 0.032292
.005	-0.018786	-0.020322	-0.020254	- 0.024081
.002	-0.012029	-0.012905	-0.012938	- 0.016037
.001	-0.008480	-0.009264	-0.009406	- 0.011653
.0005	-0.005700	-0.006625	-0.006689	- 0.008358
.0002	-0.003717	-0.004212	-0.004321	- 0.005457
.0001	-0.002476	-0.003037	-0.003226	- 0.003956

X = 73.03

m	0°	15°	25°	35°
0.1	-0.390416	-0.432002	-0.460819	-0.518252
0.05	-0.378162	-0.388153	-0.424442	-0.459697
0.02	-0.291218	-0.295516	-0.323138	-0.342678
0.01	-0.221829	-0.229120	-0.247756	-0.260292
0.005	-0.165040	-0.172094	-0.184633	-0.192974
0.002	-0.108746	-0.114629	-0.121971	-0.127099
0.001	-0.078572	-0.083083	-0.088306	-0.091683
0.0005	-0.056402	-0.059521	-0.063379	-0.065691
0.0002	-0.036125	-0.038412	-0.040679	-0.042134
0.0001	-0.025756	-0.027287	-0.029114	-0.030038

TABLE VII (Cont.)

	X = 89.00			
m	0^{o}	15^{o}	25^{o}	35^{o}
0.1	-0.746145	-0.830791	-0.881138	-1.010984
0.05	-0.711191	-0.799223	-0.846980	-0.974527
0.02	-0.633004	-0.705222	-0.776094	-0.892611
0.01	-0.533416	-0.590021	-0.663308	-0.762094
0.005	-0.425938	-0.468994	-0.534422	-0.613709
0.002	-0.299444	-0.328034	-0.378244	-0.434322
0.001	-0.223063	-0.243922	-0.282927	-0.324623
0.0005	-0.163334	-0.178653	-0.207965	-0.238553
0.0002	-0.106863	-0.116517	-0.136149	-0.156165
0.0001	-0.076706	-0.083718	-0.098086	-0.112380

TABLE VIII

COEFFICIENTS OF THE EMPIRICAL EQUATION

$E_{obs} = a + bT + cT^2$

X = weight percent of tetrahydrofuran

X = 8.98

m	a x 10^2	b x 10^3	c x 10^6	Standard Error
0.089050	10.86695	1.90426	-3.68755	0.00119
0.044490	39.46164	0.03532	-0.25967	0.00071
0.035190	43.27598	-0.18656	0.18243	0.00064
0.007790	83.11505	-2.66683	4.85265	0.00053
0.004620	90.79479	-3.10026	5.73599	0.00055
0.002310	185.29968	-9.44101	16.72599	0.00581

X = 18.21

m	a x 10^2	b x 10^3	c x 10^6	Standard Error
0.09440	10.40319	1.80400	-3.40445	0.00248
0.045010	3.15607	2.41728	-4.23599	0.00201
0.035600	3.10113	2.45108	-4.22001	0.00192
0.013140	4.53758	2.48898	-3.97602	0.00157
0.004670	0.38614	2.92101	-4.39029	0.00134
0.002340	0.75561	2.99972	-4.30891	0.00124

TABLE VIII (Cont.)

X = 47.20

m	a x 10^2	b x 10^3	c x 10^6	Standard Error
0.093390	138.05875	-6.64663	10.30573	0.00385
0.046650	82.41743	-2.75175	3.88285	0.00729
0.013620	139.54397	-6.46881	10.05421	0.00404
0.008170	180.91995	-9.25640	15.50091	0.00281
0.004840	55.79892	-0.58393	0.82117	0.00124
0.002420	161.45116	-7.71599	13.19719	0.00347

X = 73.03

m	a x 10^2	b x 10^3	c x 10^6	Standard Error
0.096320	105.72032	-4.46721	6.23777	0.00034
0.048110	50.09249	-0.52976	-0.39505	0.00045
0.022830	- 8.07969	3.56728	- 7.29597	0.00039
0.014040	- 40.23888	5.83925	-11.10323	0.00016
0.004990	- 92.47722	9.56694	-17.28230	0.00043
0.002500	-227.93697	18.93736	-33.09884	0.00590

TABLE VIII (Cont.)

X = 89.00

m	a x 10^2	b x 10^3	c x 10^6	Standard Error
0.098170	111.35684	-5.25294	7.44515	0.00032
0.049040	102.32608	-4.52393	6.35082	0.00035
0.023260	115.66118	-5.35789	7.97230	0.00119
0.014320	98.15925	-4.02875	5.64844	0.00226
0.002540	65.86399	-1.33844	0.80342	0.00293

TABLE IX

THE COEFFICIENTS OF THE EMPIRICAL EQUATION,

$E_o = a_o + b_o T + c_o T^2$

E_o = Standard Potential

X = weight percent of tetrahydrofuran

X	$a_o \times 10^2$	$b_o \times 10^3$	$c_o \times 10^6$	Standard Error
8.98	117.9971	- 5.8778	8.8506	0.000769
18.21	- 0.1689	1.9829	- 4.3315	0.000968
47.20	136.2621	- 6.9997	10.0999	0.003896
73.03	-151.2246	12.6655	-24.4081	0.001543
89.00	- 26.8913	4.3659	-11.9284	0.002415

TABLE X

THE RELATIVE PARTIAL MOLAL QUANTITIES, $\bar{L}_2$ AND $\bar{J}_2$. COMPUTED FROM EQUATIONS (81) AND (83).

X = weight percent of tetrahydrofuran

X = 18.21

	$\bar{J}_2$			
m	0°	15°	25°	35°
0.094400	11	12	13	13
0.013140	4.4	4.7	4.8	5
0.002340	0.25	0.26	0.28	0.29

X = 47.20

	$\bar{L}_2$		$\bar{J}_2$	
m	25°	35°	25°	35°
0.008170	772	1527	74	76
0.002420	526	958	43	44

X = 73.03

	$\bar{L}_2$		$\bar{J}_2$	
m	25°	35°	25°	35°
0.096320	3582	7867	421	435
0.022830	2210	3883	236	242
0.014040	1692	3553	183	189
0.004990	1069	2066	98	101

X = 89.00

	0°		15°		25°		35°	
m	$\bar{L}_2$	$\bar{J}_2$	$\bar{L}_2$	$\bar{J}_2$	$\bar{L}_2$	$\bar{J}_2$	$\bar{L}_2$	$\bar{J}_2$
0.04904	1656	230	5205	243	7677	251	10233	260
0.014320	1395	221	4807	233	7182	243	9639	250
0.002540	514	160	2986	169	4707	175	6488	181

temperatures. Here also the E^o values used for the calculations are those listed in Table IV.

The secondary medium effects of hydrochloric acid were calculated using equation (42) from the values of the mean activity coefficients of hydrochloric acid in tetrahydrofuran-water mixtures as well as the values given for hydrochloric acid in the aqueous system. Table VII represents the values of the secondary medium effects for each system at four different temperatures.

In order to calculate the relative partial molal quantities, for example, $\bar{L}_2$ and $\bar{J}_2$, the electromotive force data (E_{obs} and E^o) were expressed by the following two quadratic equations,

$$E_{obs} = a + bT + cT^2 \qquad \ldots.78$$

and

$$E^o = a_o + b_oT + c_oT^2 \qquad \ldots.79$$

in which T represents the absolute temperature in degrees Kelvin. Four observations could be made in determining the coefficients of the above equations by means of curve fitting technique, because only four different temperatures were used in our studies. E_{obs} were chosen at selected molalities and were fitted with the corresponding temperature. The coefficients of the equation (78) are given in Table VIII; whereas, those of equation (79) are listed in Table IX.

The relative partial molal heat content, $\bar{L}_2$, and the relative partial molal heat capacity, $\bar{J}_2$, were calculated by means of computer at selected molalities and at each temperature with the use of the

coefficients given in Tables VIII and IX. The values of $\bar{L}_2$ and $\bar{J}_2$ are given in Table X.

CHAPTER V

DISCUSSION AND CONCLUSIONS

The experimental data for the electromotive forces of the galvanic cells in the mixed solvent have errors which vary according to the system under investigation. In our studies, the 8.98 and 18.21 percent tetrahydrofuran in tetrahydrofuran-water mixtures had the least error of all systems and were of the order of ±0.1 mv. The errors for each system were estimated by two factors; the reproducibility of the cells and the criteria for equilibrium. The system was considered to be in equilibrium when the readings taken over a period of about half-hour did not vary more than 0.1 mv. This was the criterion consistently used to determine the attainment at equilibrium; however, the reproducibility differed. As the concentration of tetrahydrofuran was increased, the errors in electromotive force measurements were correspondingly larger, e.g., in 47.20, 73.03, and 89.00 percent of tetrahydrofuran, the errors were estimated to be ±0.4 mv, ±0.9 mv and ± several millivolts, respectively.

The molalities of the various solutions in different mixed-solvent systems were calculated from the volumetric data and the appropriate density data. Special care was taken in the preparation of the solutions to minimize the error which was approximately as high as three parts per thousand particularly for 73.03 and 89.00 percent tetrahydrofuran.

A thorough examination of the data listed in Table I evidently

points out the trends, that, in each system and at every temperature, there is an increase in the value of E_{obs} with the corresponding decrease in molality of hydrochloric acid. Furthermore, for cells of approximately the same hydrochloric acid concentration, a decrease in the values of E_{obs} results from an increase in the tetrahydrofuran composition of the mixed solvent. It should be pointed out that there is no regular trends in the E_{obs} values with a change in temperature except for given molalities of a given solvent composition.

The quantity, E', which is equal to $E_{obs} + \frac{2RT}{F} \ln m$, decreases with decreasing acid concentration, and also decreases with the increase in temperature at the same acid concentration. This decrease is consistent throughout in tetrahydrofuran-water mixtures.

A number of possible explanations may be given for the error encountered in E^{o}. The first source of error lies in the determination of the quantity $E_{obs} + \frac{2RT}{F} \ln m$; whereas, the second one is in the actual extrapolation process.

The errors involved in transforming the values of the measured electromotive force to values corresponding to a hydrogen partial pressure of one atmosphere result from making some assumptions regarding the behavior of the mixed solvent system. In our studies, it appears that the difference between the values of the E_{obs} and those of the original electromotive force is in the hundredth of millivolt, suggesting thereby that any assumption made on the ideal behavior of the solvent would be negligible since it lies beyond the

actual error in the measurements. However, in the preparation of the solutions, an error of about 0.2 percent in the molality would produce an error of approximately 0.0001 in the term, $\frac{2RT}{F}$ ln m. The maximum error in the term, $E_{obs} + \frac{2RT}{F}$ ln m, found in our investigations for 8.98 and 18.21 percent tetrahydrofuran was ±0.2 mv; whereas, for 47.20, 73.03 and 89.00 percent tetrahydrofuran solution, the errors were estimated to be ±0.5 mv, ±1.0 mv and ± several millivolts, respectively.

The error encountered in the determination of E^{o} by the extrapolation process is difficult to assess at the present time. A comparison of the results of extrapolations carried out by other means and the results obtained by using the curve fitting technique would be very helpful, but are not available at the present time. However, some preliminary work is under way in our laboratory for this type of comparison. A thorough examination of the figures 2 through 6 shows that the curvature of the plot becomes more pronounced as the concentration of the trtrahydrofuran composition is gradually increased. Any graphical extrapolations will cause a high degree of error particularly along a curved portion of the plot. Furthermore, the experimental points in the graph, which correspond to the lower concentrations or more precisely to the lower molalities of acid in the mixed solvents, are less reliable. As was pointed our previously, these were the most difficult measurements to make. In order to minimize the error, as far as practicable, in this extrapolation, the method of least square was applied to find out an empirical equation which fit the experimental data. The fundamental assumption

which was made in connection with the use of this technique was that there would not be any anomalies or discrepancies between the extrapolated behavior and apparently known behavior of the system.

From the above discussions it is evident that the greatest source of error encountered in E^{o} can be attributed to the value of $(E_{obs} + \frac{2RT}{F} \ln m)$. The E^{o} values are given in Table IV, taken directly from the computer. The errors in E^{o} values corresponding to 8.98 and 18.21 percent tetrahydrofuran are estimated to be ± 0.1 mv. For the 47.20, 73.03 and 89.00 percent solutions, the error would be approximately ± 0.6 mv; ± 1.0 mv and $\pm$ several millivolts, respectively.

A comprehensive discussion of the mean activity coefficients and other thermodynamic properties of hydrochloric acid, computed from electromotive force methods in various mixed solvents have been made by different investigators. The values of the mean activity coefficients of hydrochloric acid in dioxane-water mixtures (3), glycerol-water (3), methanol-water (3) and ethylene-glycol-water mixtures (34) are given in the Appendix (Table A-1 through Table A-IV).

Before discussing our results in a systematic way, it is worthwhile to consider some of the important aspects of the general study of the mixed solvents by electromotive force methods. Most of the previous workers in this field have studied those systems, the dielectric constant of which have been previously determined. It has been demonstrated in Chapter II that a previous knowledge of

dielectric constant of the solvent is not necessary in order to investigate the thermodynamic properties of hydrochloric acid when the appropriate polynomial curve fitting technique is employed. In addition to this fact, it has been shown that the curve fitting technique permits us to undertake such studies to be carried out with considerable elimination of some of the errors, previously encountered in graphical extrapolation.

It will be of benefit to discuss our results obtained by means of curve fitting technique. Table V in Chapter IV contains the actual values of the mean activity coefficients of hydrochloric acid in tetrahydrofuran-water mixtures. Since the values of the term $(E_{obs} + \frac{2RT}{F} \ln m)$ are smooth with decreasing concentrations, the mean activity coefficient values are expected to increase gradually with decreasing concentrations in a given system at a given temperature. The characteristics of the variation of the activity coefficient with acid concentration and temperature are illustrated strikingly by the extensive investigations of tetrahydrofuran-water mixtures (Data in Table V). The general trends of our results are in close agreement with those obtained by Harned and his co-workers in other mixed solvents such as dioxane-water, methanol-water, etc. (9, 17-29, 37, 38). The activity coefficients at all concentrations and temperatures decrease with increasing temperature. It is a matter of importance to mention in this connection that Harned and co-workers obtained smooth values of the mean activity coefficients by a slightly different technique. They studied the cells at 5° intervals over a wide range of temperatures. The electromotive force values were then smoothed

by plotting E_{obs} values versus temperature. This type of smoothing of E_{obs} values, would, most probably, bring any values which are divergent with respect to temperature into proper order. According to Harned and Owen (3), an error of ±0.05 mv in the measured electromotive force values correspond to an error of 0.001 in the values of the mean activity coefficients. In order to estimate the degree of error in the values of the mean activity coefficients, it is found that an error of ±0.02 mv, ±0.5 mv, ±1.0 mv and ± several millivolts in the term $(E_{obs} + \frac{2RT}{F} \ln m)$ for (8.98 and 18.21), 47.20, 73.03 and 89.00 percent tetrahydrofuran would cause an error of 0.004, 0.010, 0.020 and 0.040 in the activity coefficient values, respectively. In our studies, there is a general trend in the values which fall within the limit of experimental error, and hence no corrections were made. The mean activity coefficient values of hydrochloric acid in pure water are always larger than those of mixed-solvents at the same concentration. The obvious reason for this is the deviation from ideality where there are no ionic associations or interactions. Addition of an organic solvent of lower dielectric constant to a solution of hydrochloric acid reduces the dielectric constant of the mixed solvent, in other words, solvent-solute interactions are increased. In our investigations, it is seen that in the 8.89 and 18.21 percent tetrahydrofuran mixtures (Table V), the result is very similar to that in water proving thereby that there is no appreciable ionic association. In the 47.20 percent mixtures, there is evidence for ionic association, although this effect is barely noticeable. For 73.03 percent tetrahydrofuran solutions,

interactions appear to be present to a considerable extent. In the 89.00 percent tetrahydrofuran mixtures, hydrochloric acid shows the characteristic behavior of a weak electrolyte.

Table VI represents the values of the primary medium effects of the tetrahydrofuran-water mixture upon hydrochloric acid and were calculated by means of equation (37A). The primary medium effect, as already defined, is simply the mean activity coefficient of hydrochloric acid measured at infinite dilution in the mixed solvent referred to unit value at infinite dilution in pure water. Addition of small amount of tetrahydrofuran doe. not appreciably change the behavior of the medium upon the ions at infinite dilution. However, as the concentration of the organic solvent increases, the medium has a greater effect upon ions since more energy is required in transferring hydrogen ion and chloride ion from infinite dilution in the aqueous state to infinite dilution in the mixed solvent.

The secondary medium effects were calculated by using equation (42) and are given in Table VII. The characteristics of this effect in tetrahydrofuran-water media seems to be normal, and conforms to a pattern similar to that found by other investigators (2) in the studies of various mixed solvent systems.

The relative partial molal heat content, $\bar{L}_2$, and the relative partial molal heat capacity, $\bar{J}_2$, were calculated by means of equations (81) and (83) with the appropriate coefficients given in Table VIII and IX. The calculation of heat data from electromotive force measurements is very sensitive to experimental errors, the source of which has been discussed in Chapter II. As was previously pointed out, the activity

coefficients at all concentrations and temperature decrease with the increase in temperature, consequently, the relative partial molal quantities, $\bar{L}_2$ and $\bar{J}_2$ are always positive. A partial list of the values which follow almost the same general trends as those of dioxane-water are given in Table X.

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APPENDICES

TABLE A-I

VALUES OF THE MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN DIOXANE-WATER MIXTURES (3).

X = weight percent of dioxane

X = 20

m	0°	10°	25°	30°
0.1	0.736	0.729	0.720	0.716
.07	.759	.753	.740	.740
.05	.780	.774	.763	.762
.02	.835	.830	.821	.820
.01	.872	.869	.862	.861
.007	.889	.886	.880	.880
.005	.902	.900	.896	.895

X = 45

m	0°	10°	25°	30°
0.1	0.579	0.566	0.547	0.540
.07	.605	.593	.577	.570
.05	.637	.624	.607	.600
.02	.720	.707	.692	.686
.01	.776	.766	.753	.747
.005	.824	.817	.808	.803
.003	.849	.846	.842	.839

TABLE A-I (Cont.)

X = 70

m	0°	10°	25°	30°
0.1	0.236	0.226	0.212	0.207
.07	.259	.249	.234	.229
.05	.283	.274	.258	.253
.02	.369	.359	.342	.336
.01	.446	.436	.418	.413
.005	.530	.521	.505	.499
.003	.589	.582	.568	.563
.001	.719	.713	.700	.696

X = 82

m	5°	15°	25°	35°
0.100	0.0506	0.0465	0.0429	0.0390
0.070	0.0563	0.0521	0.0484	0.0441
0.050	0.0659	0.0603	0.0560	0.0513
0.020	0.0946	0.0878	0.0822	0.0757
0.010	0.1259	0.1176	0.1105	0.1023
0.005	0.1674	0.1561	0.1479	0.1380
0.003	0.2067	0.1914	0.1818	0.1708
0.002	0.2432	0.2256	0.2134	0.2001
0.001	0.3063	0.2843	0.2698	0.2540

TABLE A-II

VALUES OF THE MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN ETHYLENE-GLYCOL-WATER MIXTURES AT 25°C (35).

X = weight percent of ethylene-glycol

	X			
m	10	20	40	60
0.1	0.770	0.764	0.750	0.717
.05	0.805	0.799	0.791	0.763
.02	0.851	0.845	0.843	0.820
.01	0.871	0.878	0.876	0.858
.005	0.897	0.911	0.908	0.892
.002	-----	0.942	0.939	0.926
.001	-----	0.959	0.957	0.946

TABLE A-III

VALUES OF THE MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN GLYCEROL-WATER MIXTURES (3).

N_2 = mole fraction of glycerol

m	$N_2 = 0.01$ 25°	$N_2 = 0.05$ 25°
0.1	0.798	0.775
.05	0.826	0.810
.02	0.873	0.858
.01	0.902	0.885
.005	0.924	0.898
.002	0.951	-----

TABLE A-IV

VALUES OF THE MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN METHANOL-WATER MIXTURES AT 0°, 25°, AND 40°C (3).

N_2 = mole fraction of methanol

$N_2 = 0.0588$

m	0°	25°	40°
0.1	0.790	0.780	0.772
0.05	0.825	0.819	0.812
0.02	0.872	0.866	0.861
0.01	0.901	0.897	0.893
0.005	0.926	0.922	0.919
0.002	0.951	0.948	0.946
0.001	0.964	0.962	0.961

$N_2 = 0.1233$

m	0°	25°	40°
0.1	0.771	0.762	0.751
.05	0.814	0.806	0.798
.02	0.862	0.856	0.850
.01	0.893	0.888	0.884
.005	0.919	0.915	0.912
.002	0.946	0.943	0.941
.001	0.961	0.959	0.957

VITA

Rabindra Nath Roy was born in Durgapur, India on July 31, 1939. He passed the School Final Examination in 1954, from Bhiringi T. N. Institution, West Bengal, India. In September of 1954, he attended Asansol College and received the Intermediate of Science diploma in 1956 from Calcutta University. In August of that year, he enrolled in Jadavpur University, Calcutta, and graduated with a Bechelor of Science degree with Honours in Chemistry in 1959 and Master of Science degree in Chemistry in 1961.

Immediately after graduation, he was awarded a Fellowship for his Ph.D. degree by the Indian Department of Health. He carried out research under the scheme for about a year. Mr. Roy enrolled in the Graduate School of Louisiana State University as a Graduate Teaching Assistant in February, 1963 and is now a candidate for the degree of Doctor of Philosophy.

EXAMINATION AND THESIS REPORT

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Major Field: Chemistry

Title of Thesis: The Activity and Other Thermodynamic Properties of Hydrochloric Acid in Tetrahydrofuran-Water Mixtures

Approved:

Major Professor and Chairman

Dean of the Graduate School

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Date of Examination:

July 15, 1966